

**"SYNTHESIS AND CHARACTERISATION OF
MERCURY (II) COMPLEXES WITH
MACROCYCLIC LIGANDS"**

**A
THESIS**



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IN
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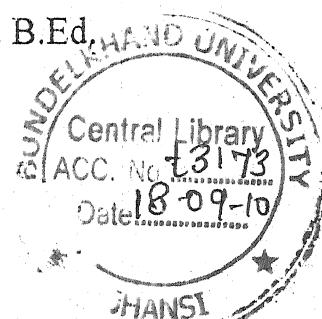
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INDIA
FEBRUARY 2008

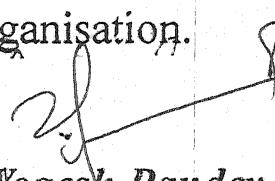
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Date : 19.02.2008

CERTIFICATE

Certified that the work embodied in this entitled
**“Synthesis and characterisation of Mercury (II)
complexes with macrocyclic ligands”** is the result of
original researches carried out by *Miss. Vijay Bharti
Gupta ‘Seth’* under my supervision and is suitable for
submission for the award of Ph.D. degree of university
of Bundelkhand, Jhansi.

The thesis fulfil the requirement attendance as laid
down by the university research organisation.



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DECLARATION

I hereby declare that the thesis entitled "Synthesis and characterisation of Mercury (II) complexes with macrocyclic ligands" being submitted for the degree of Doctor of Philosophy to the Bundelkhand University, Jhansi (U.P.), is an innovative piece of work carried out with utmost dedication by me and to the best of my knowledge and belief it has not been submitted elsewhere.

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5. CHAPTER-V

(Result & Discussion)

- (i) Introduction 122-123
- (ii) Result & Discussion 123-126
- (iii) Experimental 126-128
- (iv) Synthesis of the Complexes 128-138
- (v) References 139-142

6. CHAPTER - VI

(Conclusion)

- (i) Conclusion 143-152
- (ii) References 153-158

CHAPTER - I

Introduction

The coordination chemistry of multidentate macrocycles has been a field of intensive research over the past many years. There is no dearth of literature on the structural, synthetic or functional aspects of macrocyclic chemistry. The first documented macrocycle possessing a pyrrole (Fig.1) sub heterocyclic ring was synthesized¹ in 1886 by **Baeyer** via the condensation of pyrrole and acetone in the presence of mineral acid. The first macrocyclic compound prepared from a diacid was dimeric ethylene succinate (Fig.2) which was reported² by **Vorlander** in 1894. Subsequently, very little work was carried out with macrocyclic diesters until 1930s. The main interest in macrocyclic diester compounds involved their use in preparation of perfumes³ **Carothers** and his co-workers⁴⁻⁵ in 1930 commenced a study of polyesters including the macrocyclic monomeric and dimeric carbons, oxalates, etc. The field of macrocyclic chemistry has undergone a rapid change after the early 1960s due to the pioneering independent contribution of **Curtis**⁶⁻⁷ and **Busch**.⁸ The coordination chemistry of these macrocyclic systems was mainly confined to those systems containing N, O and S donor atoms.

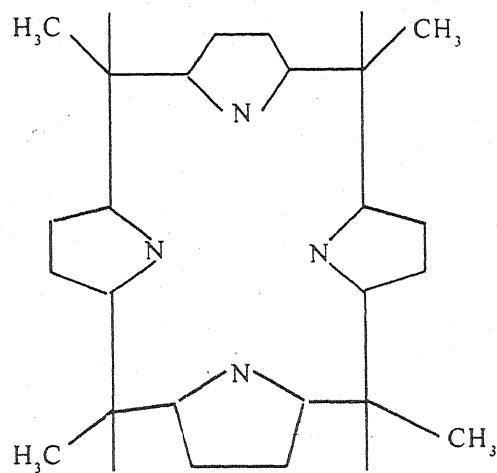


Fig - 1

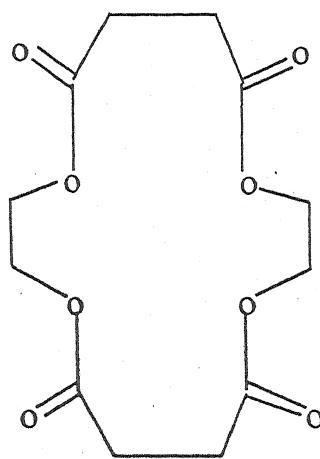


Fig - 2

A macrocycle is defined as cyclic compound having at least nine, or more, heteroatomic members and with three, or more, donor centres⁹⁻¹². They have an internal hydrophilic cavity formed by donor atoms, and an external hydrophobic framework made up of chains. The three-dimensional extension of macromonocycles in which more than one macrocycle is incorporated in the

same molecule are called macropolycycles¹³. An important feature of macrocyclic chemistry is that the design and synthesis of macrocycles with varying ring size and donor sites, with specific properties can be achieved with relative ease. The different types of macrocyclic ligands are particularly exciting because of the importance in generating new areas of fundamental chemistry and many opportunities of applied chemistry.

The macrocyclic complexes in general are found to have the following characteristics¹⁴.

- 1) They can stabilize high oxidation states that are not normally readily attainable.
- 2) They have a marked kinetic inertness both to the formation of the complexes from the ligand and metal ion and to the reverse, the extrusion of the metal ion from the ligand.
- 3) They have high thermodynamic stability and the formation constants.

The additional enhancement in stability expected from

gain in translational entropy can not be attributed to the unusual chelate effect that has been termed as the macrocyclic effect¹⁵. The differences in configurational entropy is because greater loss in entropy would be expected in the complexation of the open ligand than in the macrocyclic ligand. The macrocyclic effect has both enthalpy and entropic components as compared to the chelate effect which is largely entropic in origin. Thus for the macrocycle the donor atoms are constrained near the required coordination sites and so the ligand is pre-strained to suggest additional stability compared with the non macrocycle. The macrocyclic effect is best understood by considering the thermodynamics¹⁵⁻¹⁶ of the metal complexation reactions.

Over the past 2-3 decades an extensive series of macrocyclic ligands have been prepared and studied which are classified into various subdivisions¹³. The following types are a few of the macrocyclic ligands classified into various different subdivisions (Fig 3-16).

(i) Coronands¹⁷⁻¹⁸ (3) are macrocyclic species which contain various heteroatoms as binding sites. The complexes

of these ligands are referred to as coronates.

- (ii) Crown ethers¹⁹ (4,5) are macrocyclic polyether.
- (iii) Macroyclic polycarbonyls are cyclic ligands containing carbonyl functionalities, the macrocyclic oligoketones²⁰ (6), the polylactones²¹ (7) and the polylactams²² (8).
- (iv) Spherands²³ (9) and hemispherands²⁴ (10) are macrocyclic ligands which consist of arrangements of phenyl groups.
- (v) Calixarenes²⁵ (11), from the Greek meaning chalice and arene (incorporation of aromatic rings), are macrocyclic phenol -formaldehyde condensation products.
- (vi) Cyclodextrins²⁶ are naturally occurring cyclic oligomer of 1, 4- glucopyranosides.
- (vii) Catenands²⁷ (12) are two separate, but interlocked macrocyclic ligands.

(viii) Cryptands²⁸⁻²⁹ (13,14) are macropolycyclic receptor molecules which provide a cavity for inclusion of a variety of substrates. cryptate refers to their complexes.

(ix) Sepulchrates³⁰ (15) are polyaza macrobicycles analogous to the cryptands.

(x) Speleands³¹ (16) are hollow, macropolycyclic molecules formed by the combination of polar binding units with rigid shaping groups.

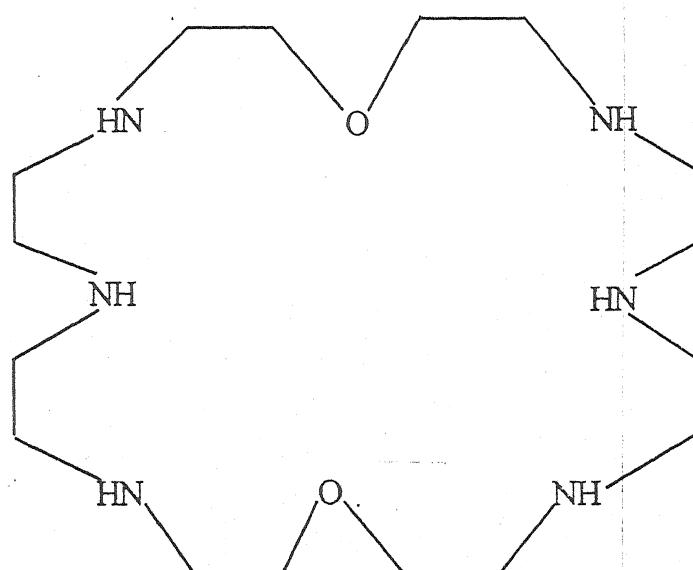


Fig. 3

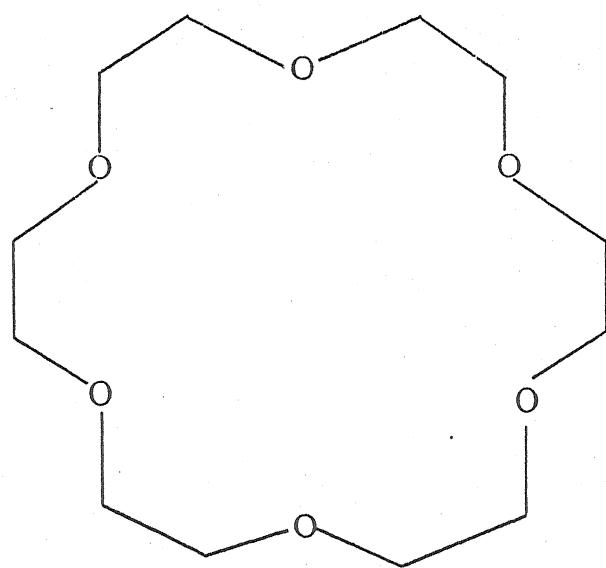


Fig. 4

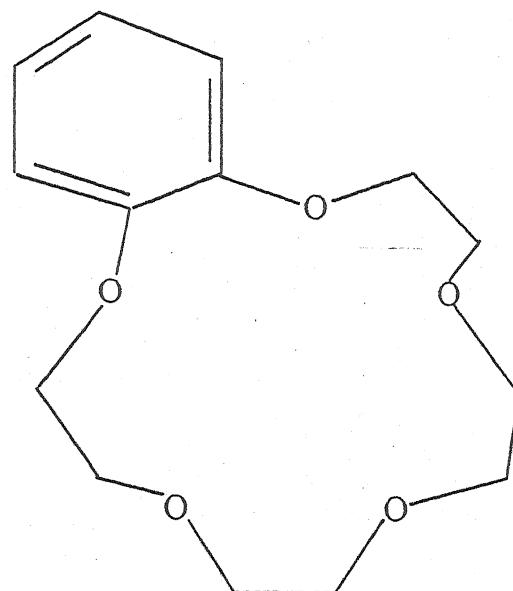


Fig. 5

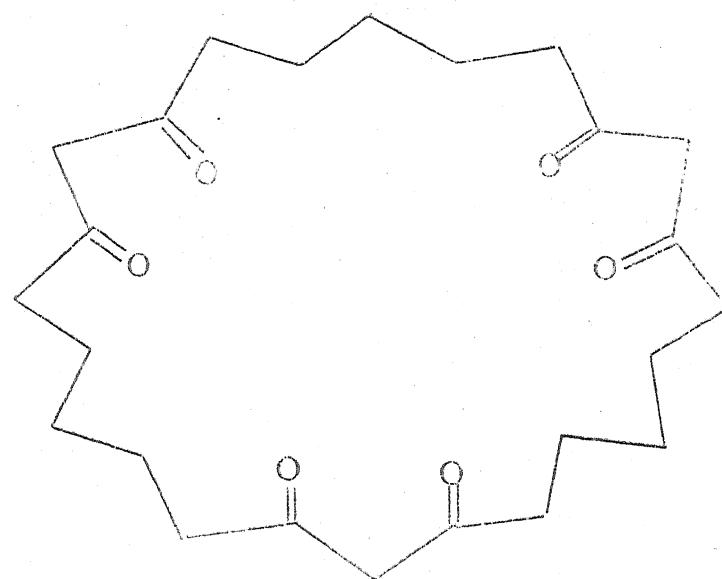


Fig. 6

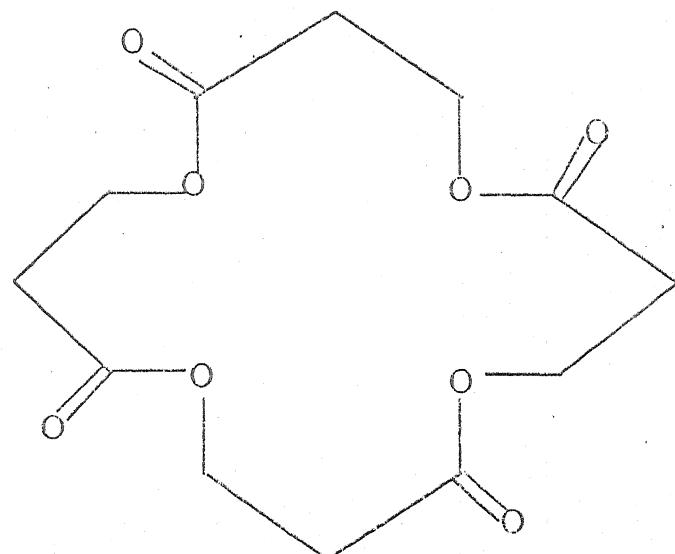


Fig. 7

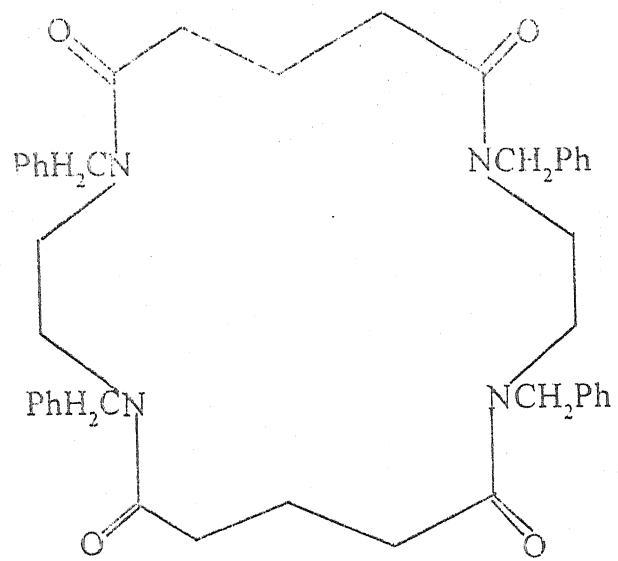


Fig. 8

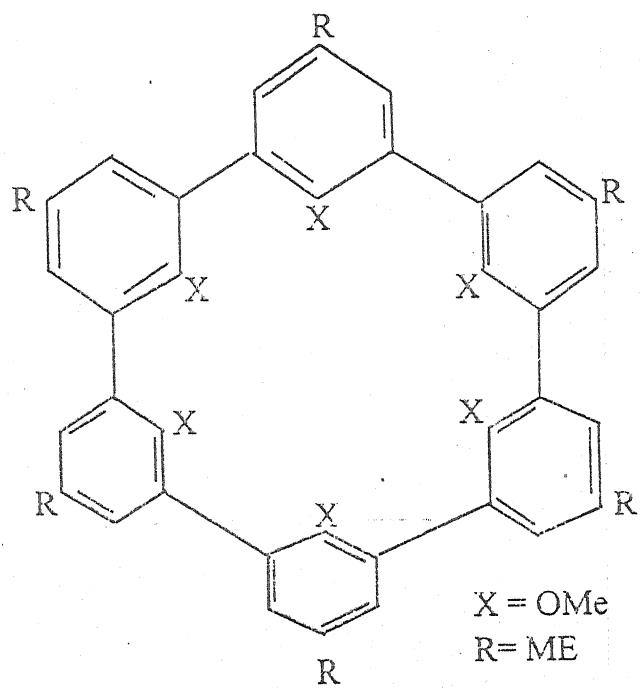
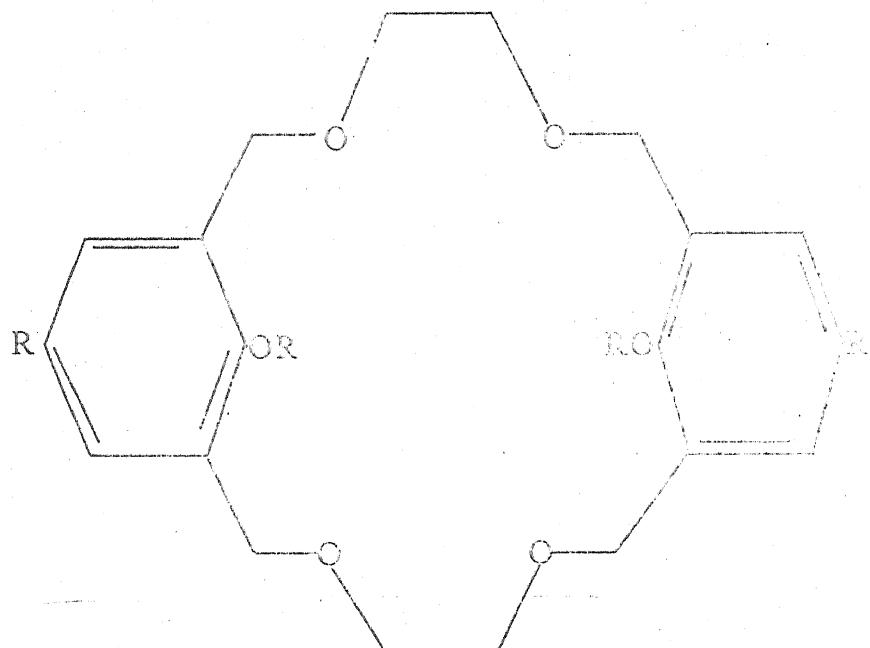


Fig. 9



$R = Me$

Fig. 10

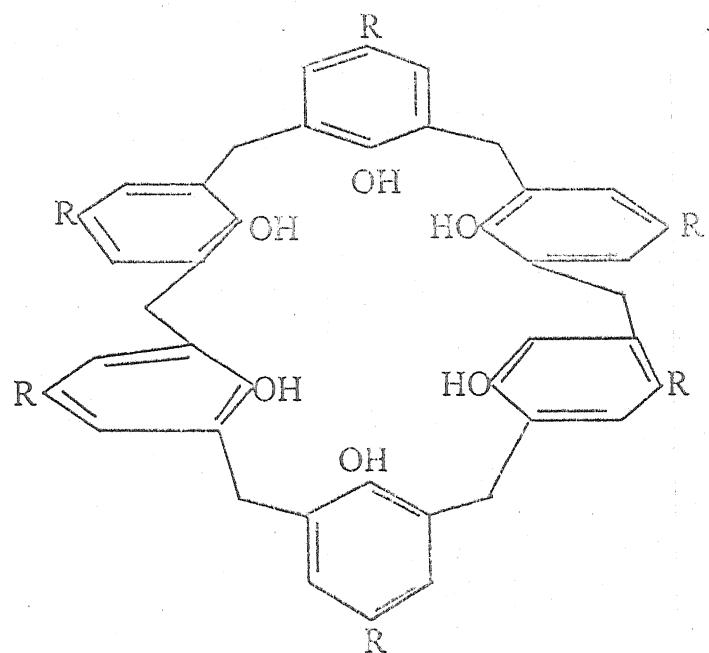


Fig. 11

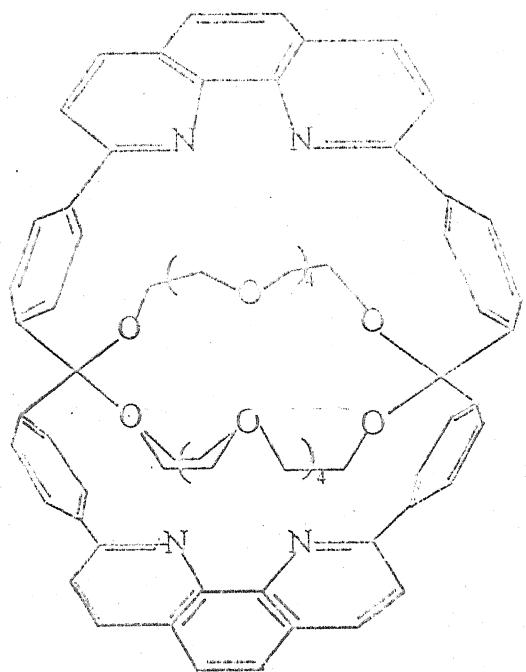


Fig. 12

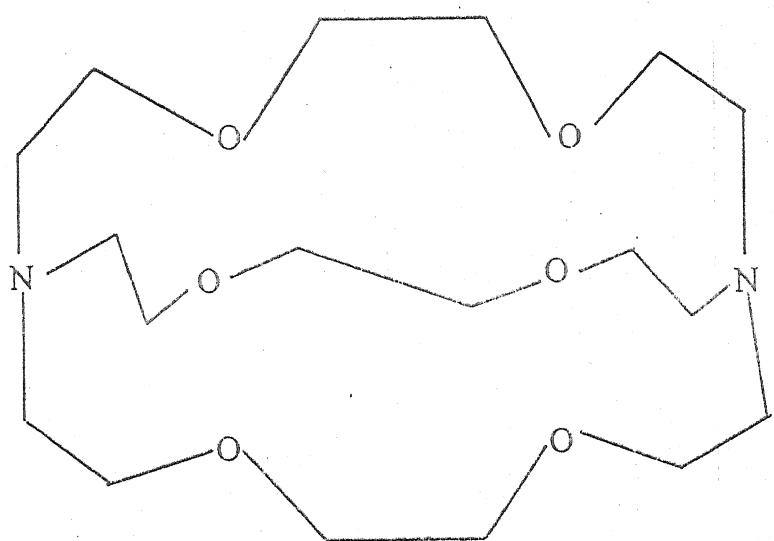


Fig. 13

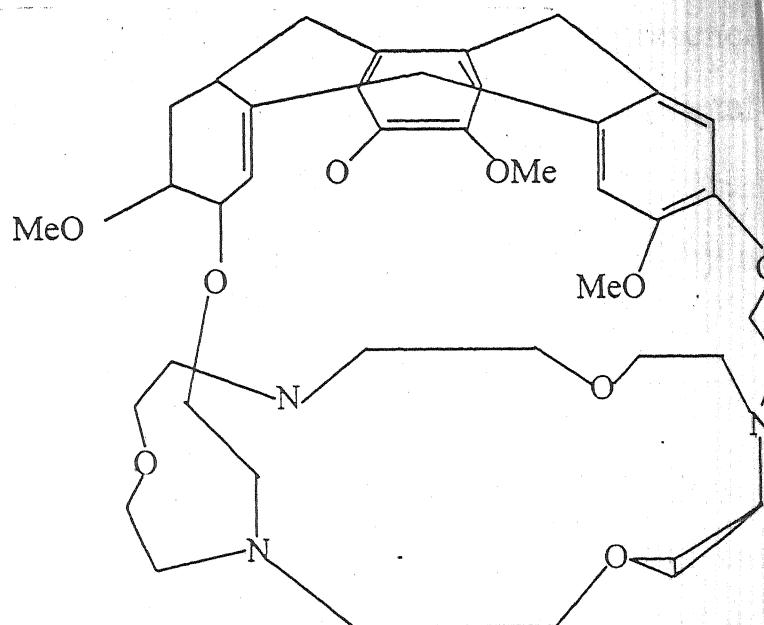


Fig. 16

The compounds shown in (Fig. 3-16) differ in type and number of ion binding sites and thus generally exhibit quite different affinities for a given ion. For example, certain cyclic polyether not only strongly bind particular alkali and alkaline earth metals but selectively bind one or more of these ions in preference to the others in each series.

There are four main approaches to prepare such systems:

- a) conventional organic synthesis of the ligands.
- b) Metal ion promoted reaction- involving condensation

of non cyclic components in the presence of suitable metal ion (in short termed as metal template procedure).

- c) Modification of a compound prepared by methods a and b.
- d) High dilution technique.

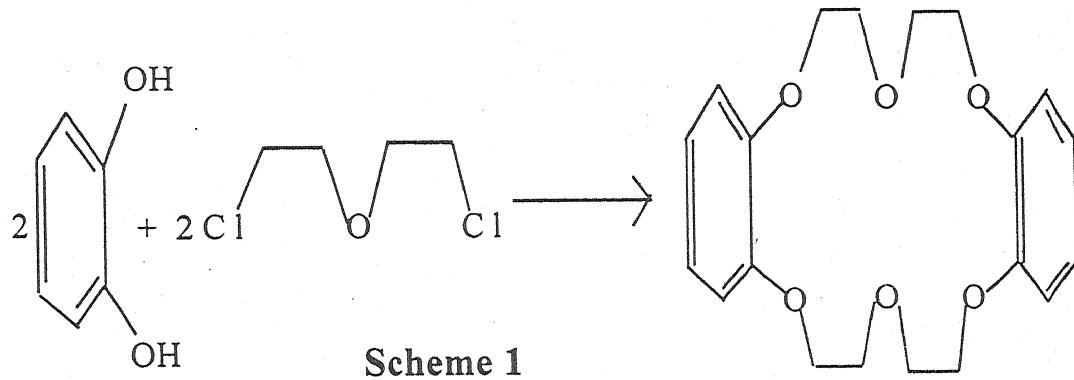
The preparation of the free macrocycles has certain advantages in many cases. The purification of the organic product may be more readily accomplished than purification of its complexes, and further the characterization by physical techniques becomes more easy. But the free macrocycles are often of low yield for the desired product and may have side reactions. To overcome this problem the ring closure step in the synthesis may be carried out under conditions of high dilution³² or another way is that a rigid group may be introduced to restrict rotation in the open chain precursors³³⁻³⁴ which facilitates cyclization. One of the most effective method for the synthesis of macrocyclic complexes involves an in situ approach where the presence of metal ion in the cyclization reaction marked increase the yield of the cyclic product. The metal ion plays an important in directing the

steric course of the reaction and this effect is termed "Metal template effect"³⁵. The metal ion may direct the condensation preferentially to cyclic rather than the polymeric products. The metal ion and the anion are important to the template process because the balance between the size of the cation and anion will determine the degree of dissociation of the metal salt in the reaction medium³⁶.

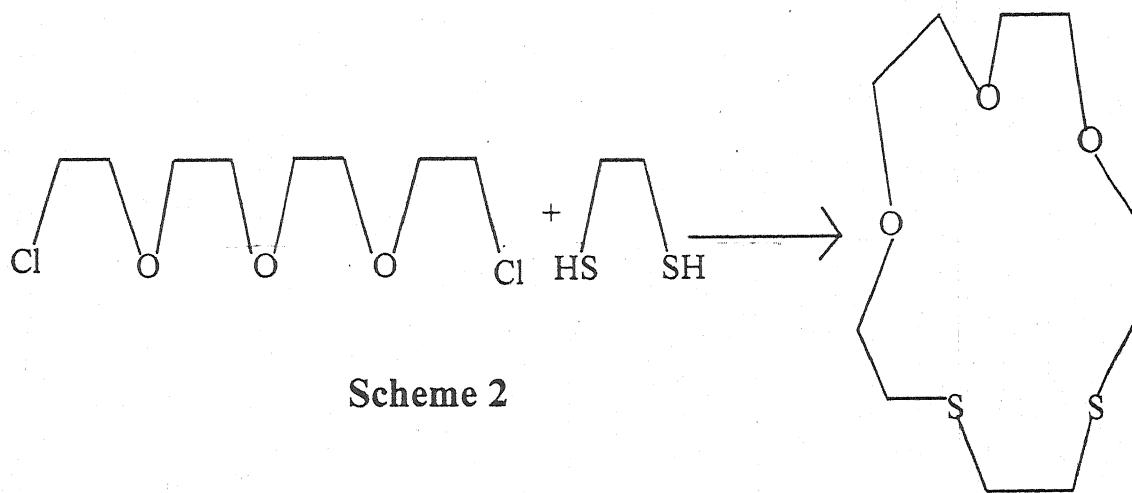
Several classes of macrocyclic ligands which include saturated polyaza macrocycles, polyoxa macrocycles, polyoxaaza macrocycles, crown ethers, cryptands, compartmental macrocyclic ligands that form mononuclear and heteronuclear complexes, pH responsive macrocycles and macrocycles containing pendant arms have been synthesized and their reactivities towards metallic substrates have been reported. These macrocyclic which contain varying combinations of aza [N], oxa [O], phospha [P] and sulpha [S] ligating atoms can be tailored to accommodate specific metal ions by the finetuning of the ligand design features. Such as the macrocyclic hole size, nature of the ligand donors, donor set, donor array, ligand conjugation, ligand substitution number and sizes of the chelate rings

ligand flexibility, and nature of the ligand backbone.

The crown poly-ethers are examples of macrocycles which have been prepared mainly by the direct synthesis¹⁹⁻³⁷ (Scheme 1) employing non template procedure. Mixed oxa-thia crowns are obtained from oligo(ethyleneglycol) dichloride reactions with dithiols³⁸⁻⁴⁰ (Scheme 2).

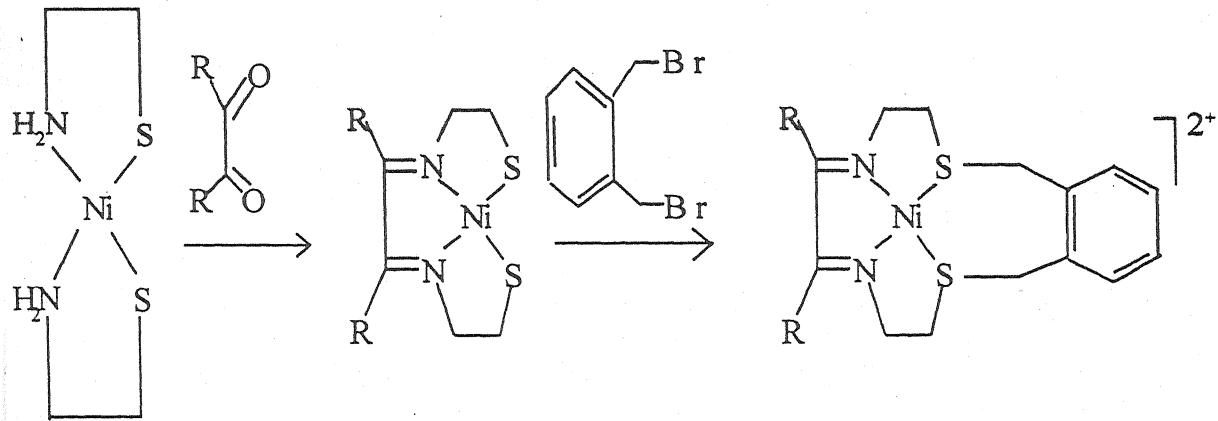


Scheme 1



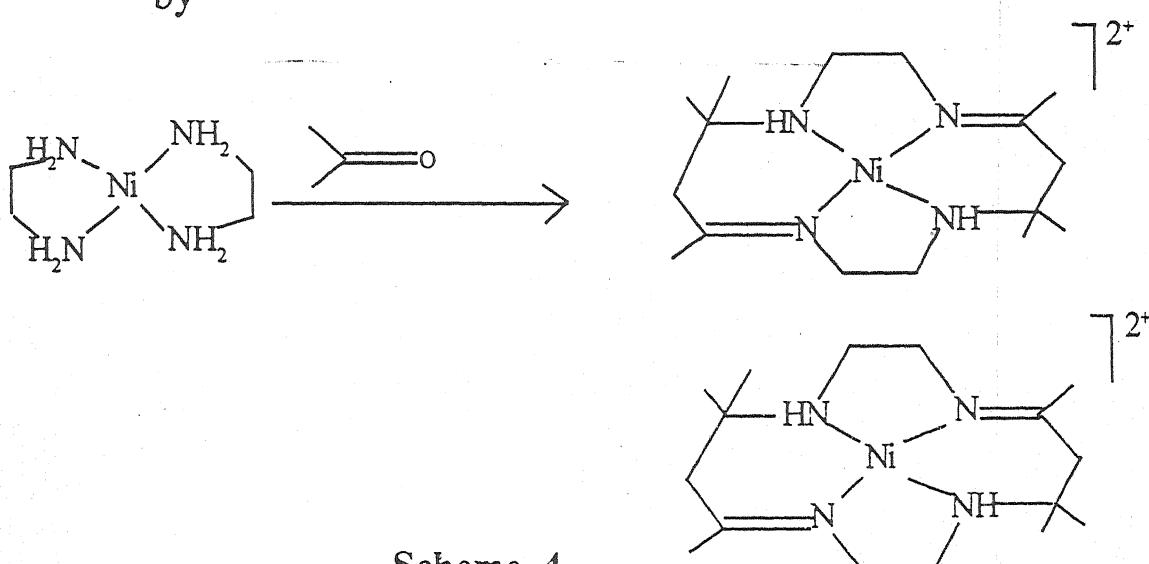
Scheme 2

The first example of deliberate synthesis of a macrocycle using template procedure was described⁴¹ by Thompson and Busch (Scheme 3), although Curtis had previously demonstrated the potential of



Scheme 3

template assembly through his observation that the reactions of $\text{Ni}(\text{en})_3(\text{ClO}_4)_2$ ($\text{en} = 1,2\text{-diaminoethane}$) and acetone yields isomeric tetraazamacrocyclic complexes⁴² of Ni(II) (Scheme 4) polythia macrocycles are obtained by

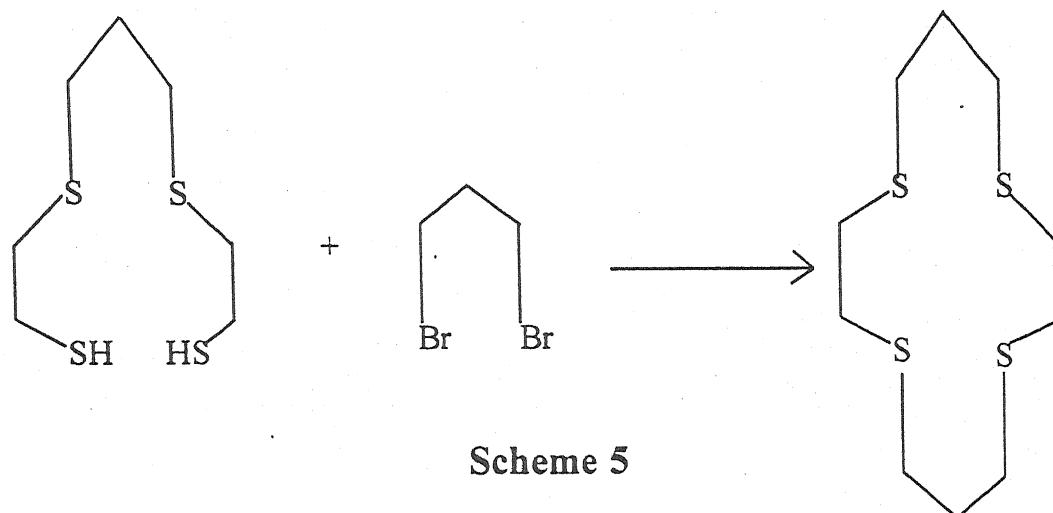


Scheme 4

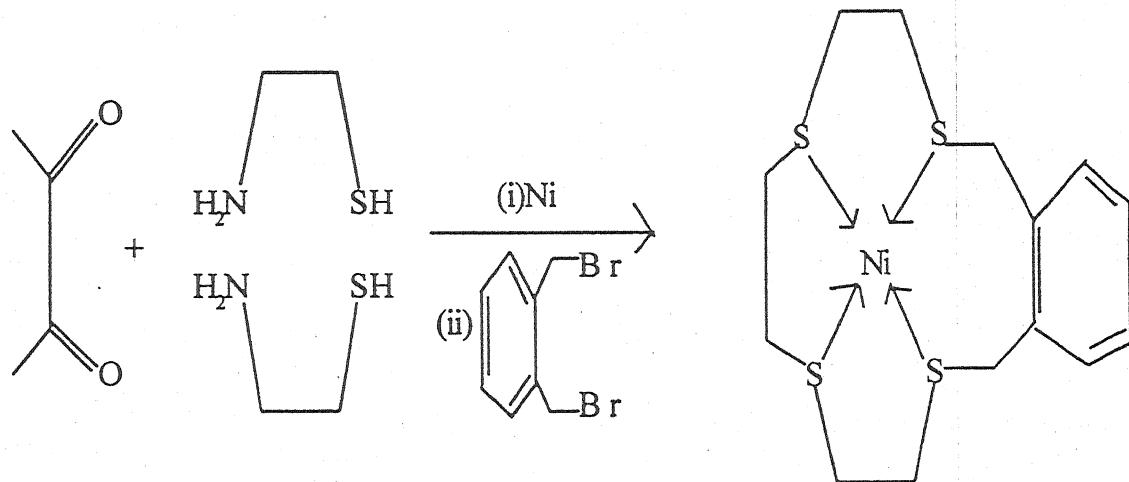
reacting an appropriate polythiane with a dibromoalkane.

The reactions are sometimes, aided by metal template^{41,43}

(Scheme 5 and 6). The phosphorous

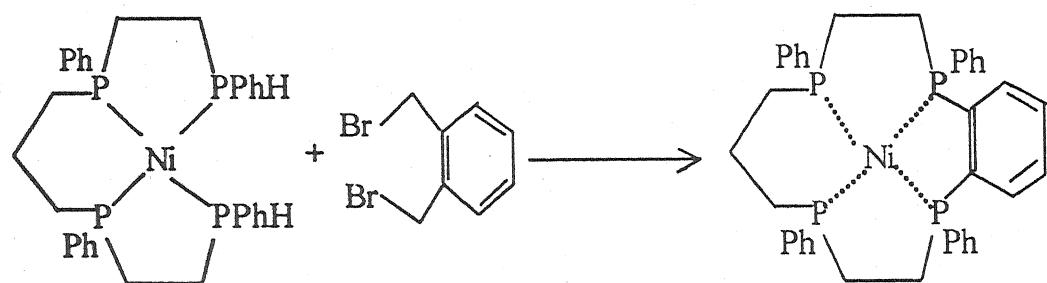


Scheme 5



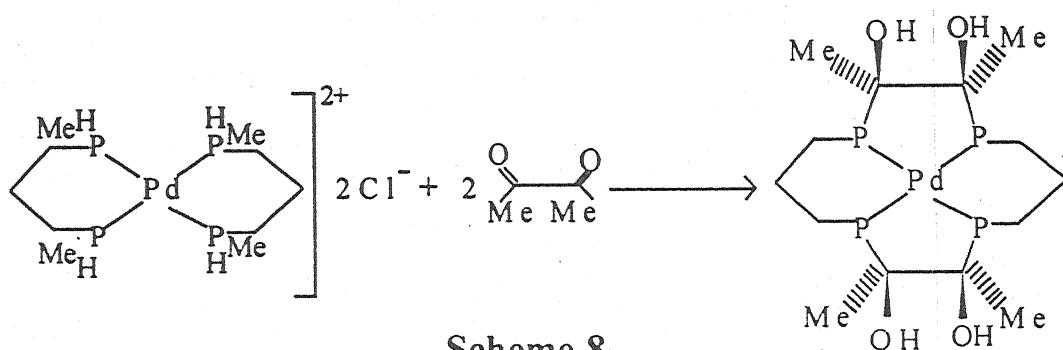
Scheme 6

macrocycles⁴⁴ are made via template condensation of coordinated polyphosphine ligands and a dibromoalkane (Scheme 7).

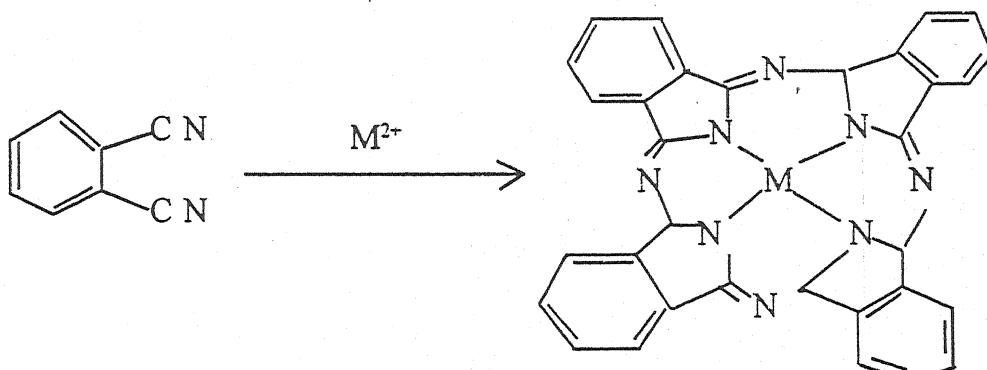


Scheme 7

Template assisted single-stage ring closure methods are also reported⁴⁵ (Scheme 8). Metal salts also facilitate the self-condensation of o-phthalonitrile to give metal-phthalocyanin complexes⁴⁶ (Scheme 9).

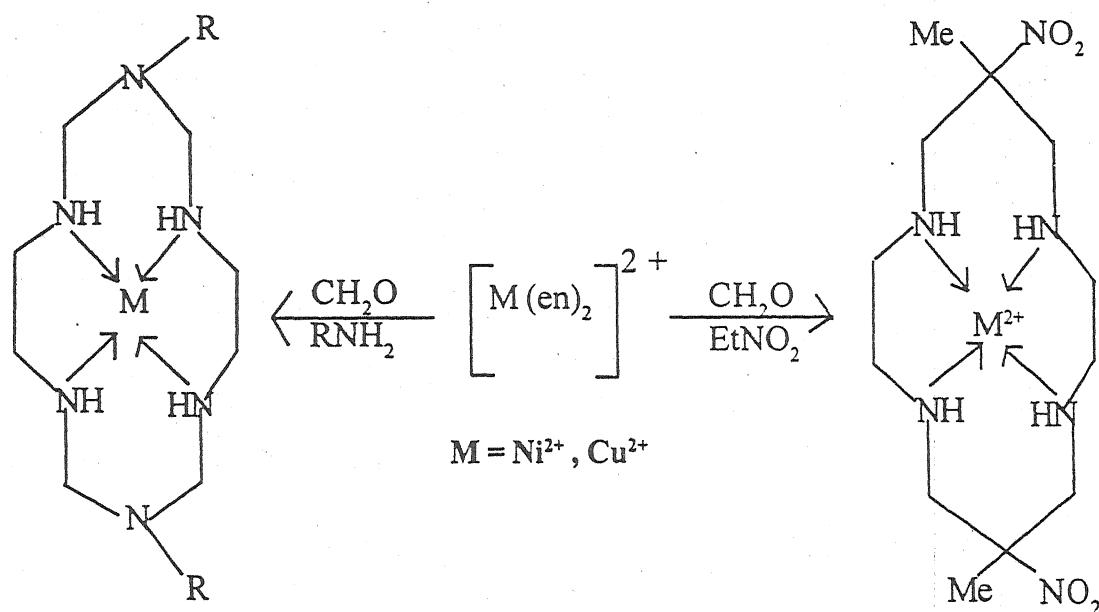


Scheme 8



Scheme 9

Schiff base condensation between a carbonyl compound and an organic diamine in the presence of a metal ion to yield an imine linkage has led to the synthesis of many azamacrocyclic complexes⁴⁷⁻⁴⁸ as illustrated below (Scheme 10). The diamine Schiff base macrocycles



Scheme 10

obtained by the condensation of one molecule each of the dicarboxyl compounds and diamine precursors have been termed “1+1” macrocycles and the tetraimine macrocycles obtained by the condensation of two molecules of the dicarboxyl compounds with the two molecules of

the diamine moiety have been termed "2+2" macrocycles as a consequence of the number of head and lateral units present ⁴⁹⁻⁵⁰. The formation of "1+1" macrocycle via intramolecular mechanism or "2+2" macrocycle via the bimolecular mechanism depends on one or more of the under given factors during the synthesis of Schiff base macrocycles.

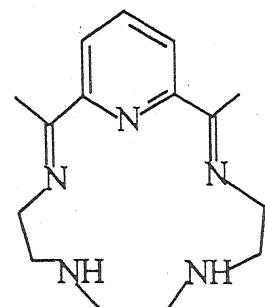
- (I) The insufficient chain length to span two carbonyl groups in the diamine will block the formation⁵¹ of "1+1" macrocycles.
- (II) A "2+2" condensation may occur⁵² if the template ion is large with respect to cavity size of the "1+1" ring.
- (III) The electronic nature of the metal ion and the requirement of a preferred geometry of the complex.
- (IV) The conformation of the "1+1" acyclic chelate.

Much of the early work featured the use of transition metal ions in the template synthesis of quadridentate macrocycles. The directional influence of orthogonal d-orbitals was regarded as instrumental in guiding the

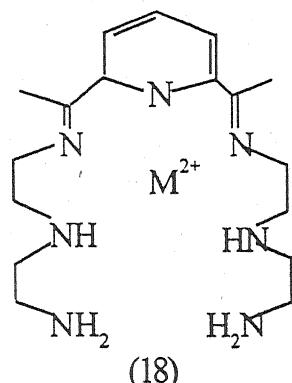
synthetic pathway. This techniques has been extended in the last decade by using organotransition metal derivatives to generate tridentate cyclononane complexes⁵³⁻⁵⁴. The synthesis of macrocyclic complexes by the metal template method was extended by the use of s-p block cations as template devices to synthesize penta and hexadentate Schiff base macrocycles⁵⁵⁻⁵⁶ and a range of tetraamine Schiff base macrocycles⁵⁷⁻⁵⁹.

The template potential of a metal ion in the formation of a macrocycle depends on the preference of the cations for stereochemistries in which the bonding d-orbitals are in orthogonal arrangements. This is exemplified by the observation that neither copper(II) nor nickel(II) acts as template⁶⁰ for the pentadentate "1+1" macrocycles (fig. 17) derived by the Schiff base condensation of 2, 6-diacetylpyridine with triethylenetetraamine, N,N¹-bis (3-aminopropyl)ethylenediamine, or N,N¹ -bis (2-aminoethyl)-1, 3-propanediamine, respectively. However, Mg²⁺, Mn²⁺, Fe²⁺, Co²⁺, Zn²⁺, Cd²⁺ and Hg²⁺ serve as effective templates leading to the formation of 7-coordinate complexes of pentagonal bipyramidal geometries (Fig.18) for Mg²⁺, Mn²⁺, Fe²⁺, Zn²⁺ and Cd²⁺

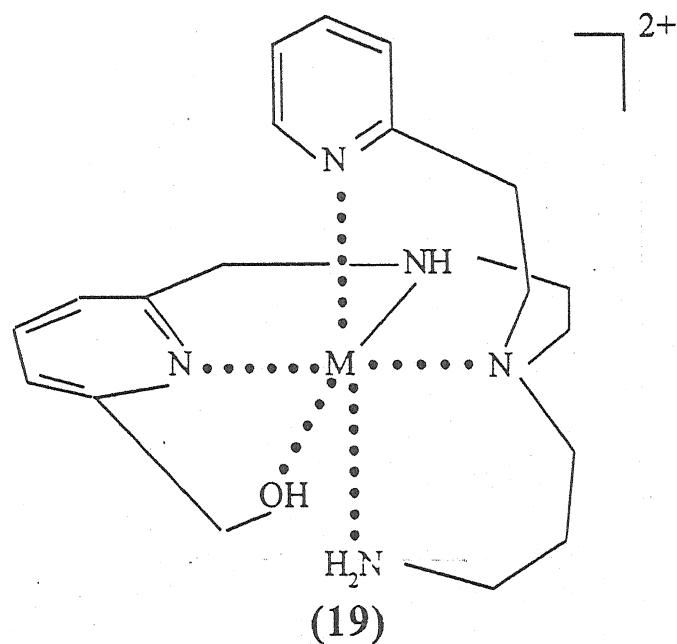
and 6-coordinate pentagonal pyramidal geometries (Fig.19) for Co^{2+} , Cd^{2+} , and Hg^{2+} ⁶¹⁻⁶³ in the synthetic pathway of macrocycles the size of cation used as the template has proved to be of much importance. The compatibility between the radius of the templating cation and the "hole" of the macrocycle contributes to the effectiveness of the synthetic pathway and to the geometry of the resulting complex. For example, cation of radius less than 0.80Å do not seem to generate complexes as shown in (Fig.19). Fenton and his co-workers⁵⁰ demonstrated cation cavity "best-fit" in the formation of Schiff base macrocycles by synthesizing oxaazamacrocycles using alkaline earth cation as templating device. The smaller metal ion favours the formation of "1+1" (Fig.20) while the large metal ion favours the formation of "2+2" macrocycles (Fig.21) as shown in Scheme 11. Among the alkaline earth cations for example only magnesium generates the pentadentate "1+1" (Fig.21) but it is ineffective in generating the hexadentate "1+1" macrocycles (Fig.22) which are readily synthesized in the presence of larger cation such as Ca^{2+} , Sr^{2+} , Ba^{2+} , and Pb^{2+} . The preference for the formation of "1+1" or "2+2" Schiff base macrocycle in the metal template condensation depended on the cations radius.



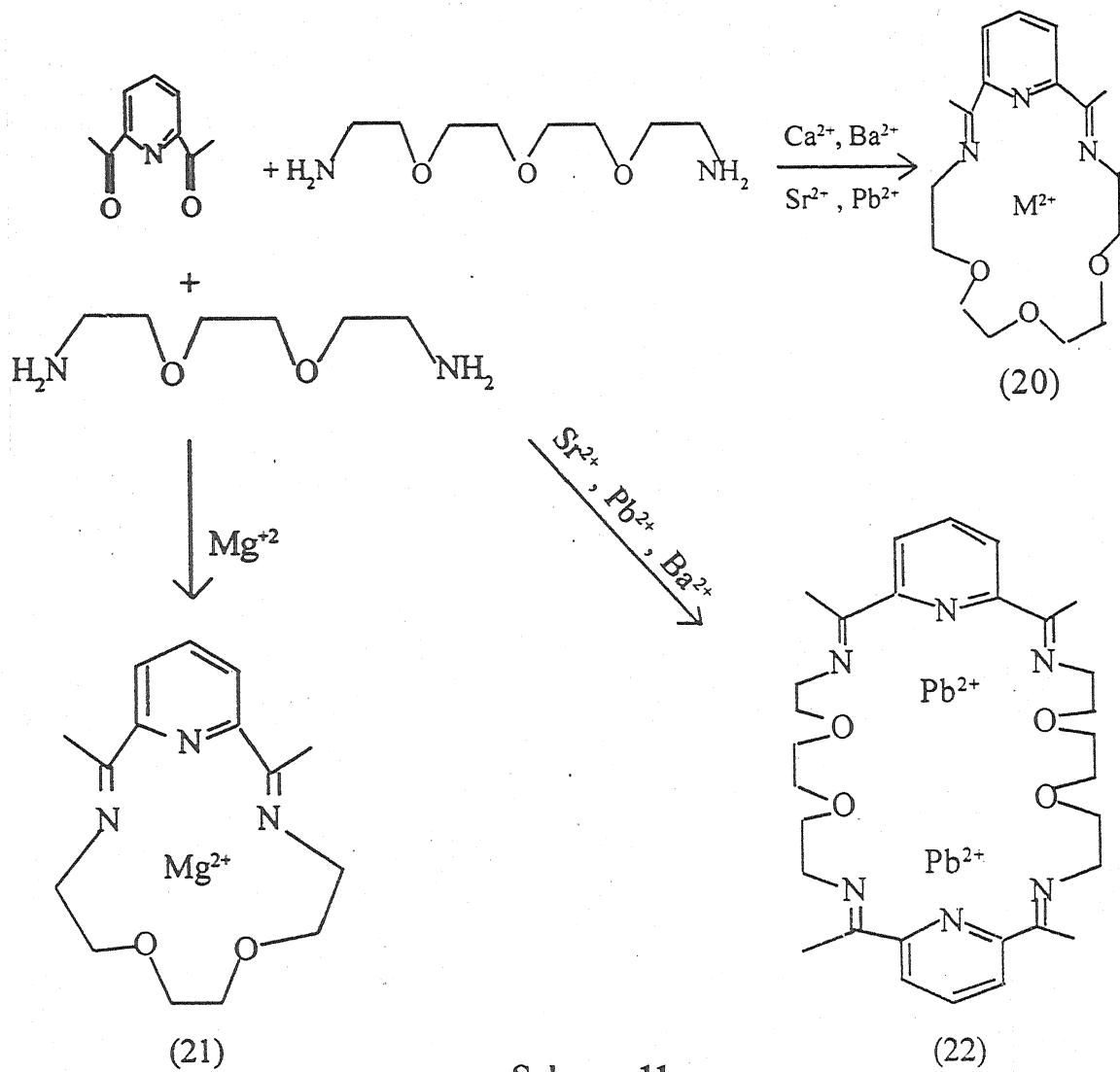
(17)



(18)



(19)



Scheme 11

A great variety of azamacrocyclic complexes have been formed by condensation reactions in the presence of metal ions (metal template). The majority of such reactions have imine formation as the ring closing step. Tetraazamacrocycles with 14- and to a lesser extent 16-membered ring predominate. While amongst the various first transition series $\text{Ni}(\text{II})$ and $\text{Cu}(\text{II})$ are the most

widely active metal ions used in the template procedure⁶⁶. The design of the ligand capable of forming stable metal complexes would not only allow further study of the coordination properties of the metal ion but also would enable to exploit in detail certain important emerging properties of these complexes. The design of macrocyclic Schiff bases have provided their potential use as metal specific ligand allowing incorporation of even two or more metal ions simultaneously.

Polyazamacrocyclic ligands are found to be very versatile ligands due to their capability of forming stable metal complexes⁶⁷. Metal coordination by polyazamacrocycles has been widely investigated in the design of selective complexing agents, ionophores and catalysts⁶⁸⁻⁶⁹. These compounds have also been used to mimic the active centre of important metal containing enzymes⁷⁰⁻⁷¹. Moreover, polyamine macrocycles constitute an excellent basis for the study of molecular recognition of different kinds of substrates, such as inorganic or organic cations, anions, and neutral molecules⁷²⁻⁷⁴. Among the polyazamacrocycles tetraazamacrocycles are extensively studied. Shakir and co-workers have reported⁷⁵⁻⁷⁸ the

synthesis and characterization of a large number of tetraazamacrocyclic complexes formed by the template condensation.

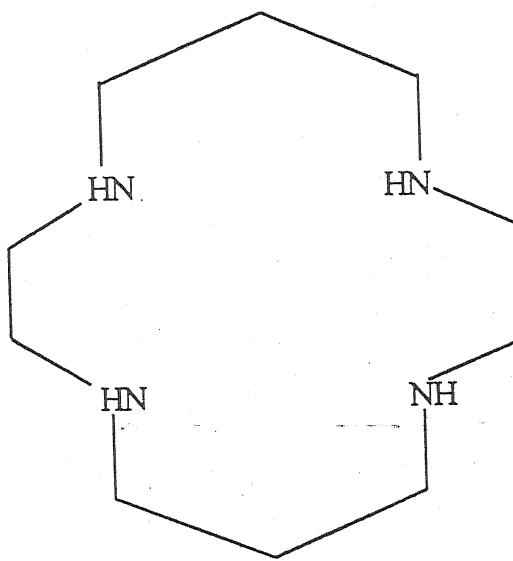
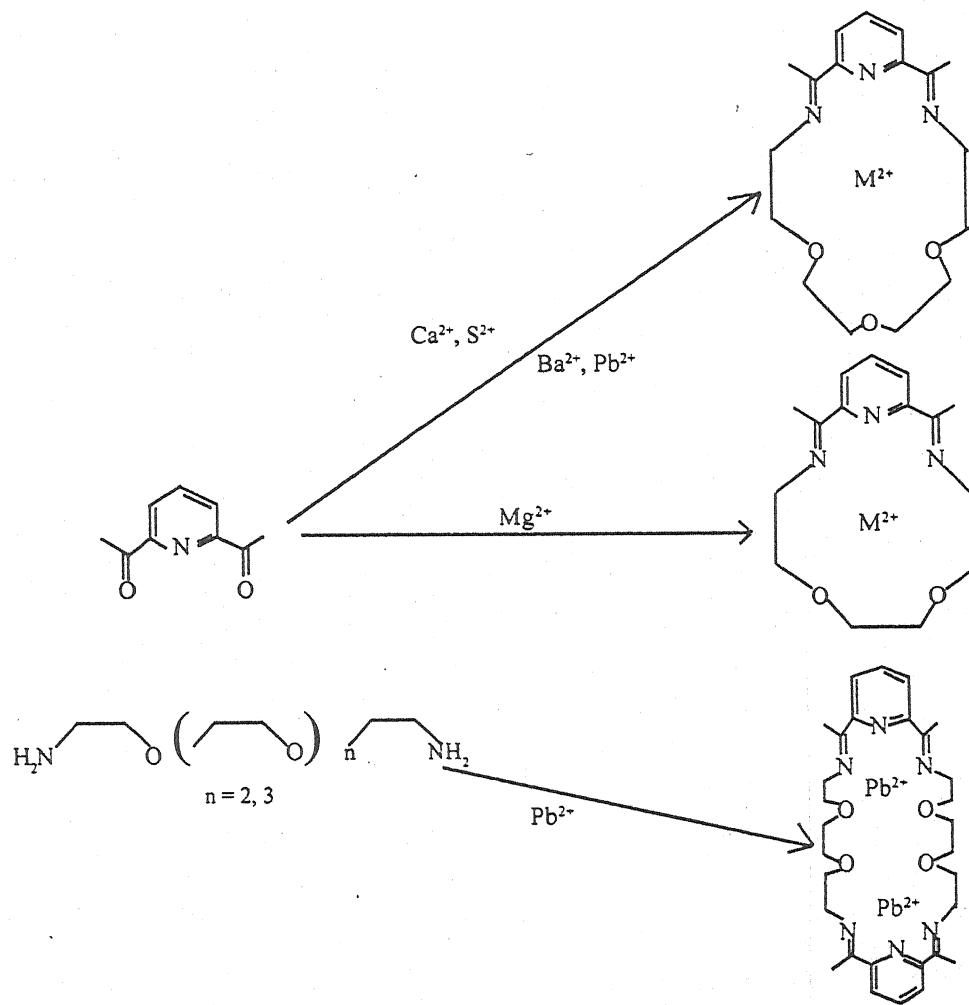


Fig. 23

It has been generally found that for the larger Schiff base macrocycles the transition metal cations are ineffective as templates⁷⁹. Transmetallation reactions⁸⁰⁻⁸³ have been successfully employed for such macrocycles. This approach has been particularly successful when applied to the generation of di-nuclear Cu(II) complexes of tetraamine Schiff base macrocycles. The latter have been used as speculative models for the bimetallobiosites in cupro-

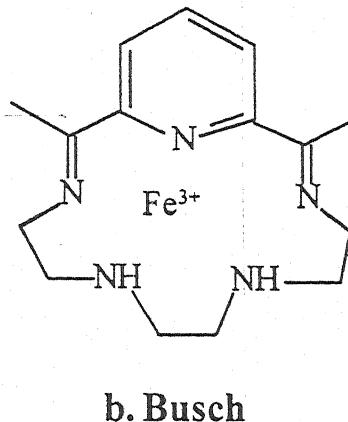
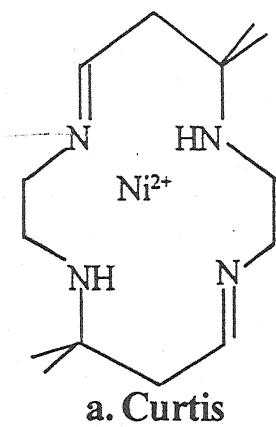
proteins such as haemocyanin and tyrosinase⁸³. The size of the cation used as the templates has proved to be of importance in directing the pathway for the Schiff base systems (Scheme 12).

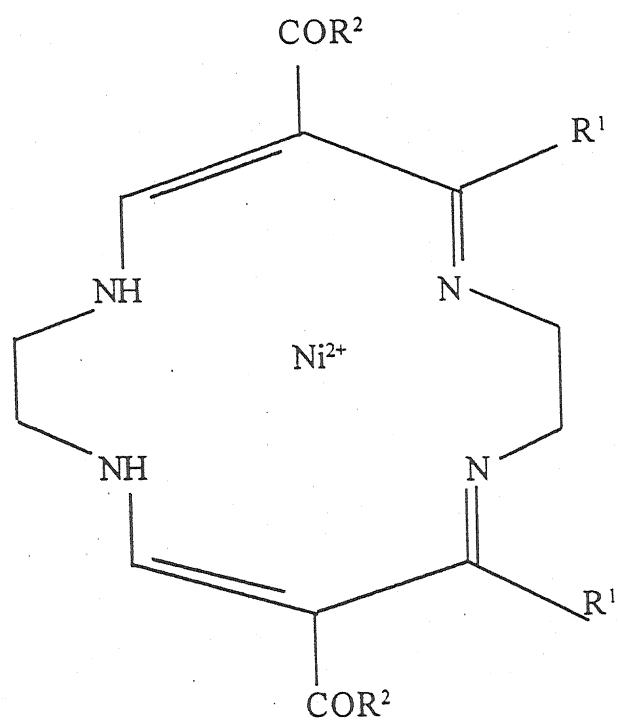


Scheme 12 Schiff base macrocycle synthesis in the presence of non-transition metal templates

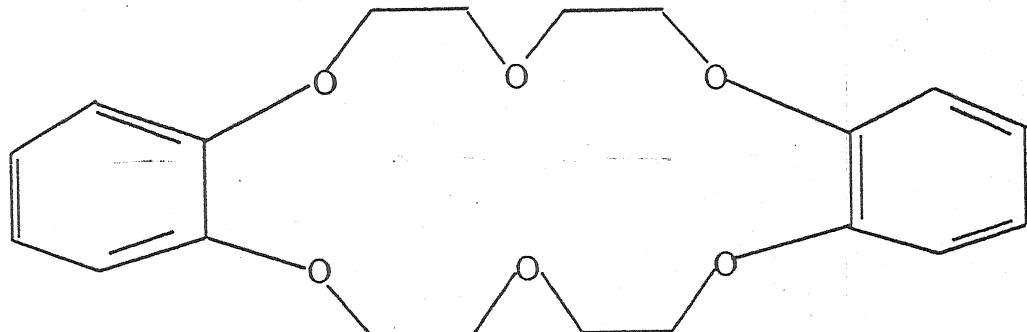
Macrocycles containing Schiff base linkages have provided three of the corner stones upon which supramolecular chemistry has been built (Fig.24 a-c).

The earliest example of a synthetic macrocyclic ligand containing an imine linkage stems from the work of **Curtis** and was derived from the mixed -aldol condensation of acetone with nickel(II) ethylenediamine complexes⁸⁴. In 1964 **Curry and Busch** reported the iron(II) templated condensation of 2,6-diacetylpyridine with triethylenetetraamine to give iron(III) complexes of a pentaazadiaminomacrocyclic⁸⁵. It was shown by **Jager** in 1964 that the reaction of β ketoiminato complexes with 1,2 diaminoethane gave metal complexes of a tetraazadiimino macrocycle⁸⁶. The fourth cornerstone (Fig.24d) was added by **Pederson** with his discovery of the cyclic or "crown" polythers⁸⁷. In this case the metal cation was not retained by the product and so it was proposed that the role of the metal was to organize the transition state, which preceded formation of the macrocycle.





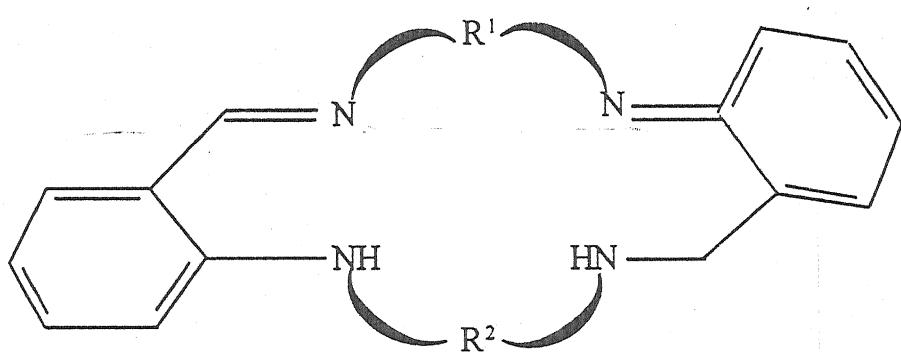
c. Jager



d. Pedersen

Fig. 24 The cornerstone macrocycle

Lindoy and co-workers have developed design strategies for new macrocyclic ligand systems which are able to recognize particular transition and post-transition metal ions. They have prepared and studied the discrimination of metal ions by ligand and by following the occurrences of "structural dislocation" along a series of closely related (Fig.25 and Fig.26) mixed donor ligand system.



$$R^1 = R^2 = (CH_2)_2 \cdot (CH_2)_3$$

Fig. 25

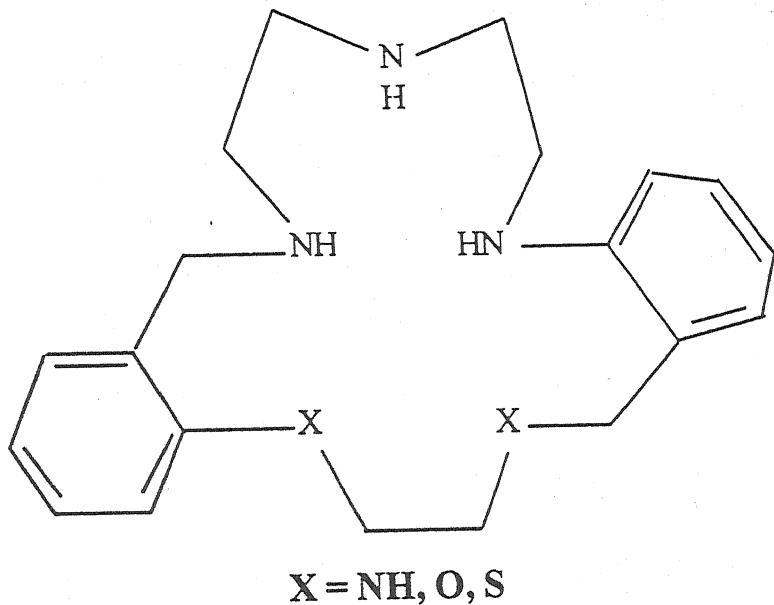


Fig. 26

The chemistry of synthetic macrocyclic polyamines and macrocyclic dioxopolyamines has been drawing much interest⁸⁸⁻⁹¹. These macrocycles form much more stable and selective complexes with various transition metal ions than do open chain analogues having the same donor arrangement. The metal complexes of the 14- membered cyclic tetraamine 1, 4, 8, 11- tetraazacyclotetradecane (Fig. 27) represent reference systems⁹²⁻⁹³ in the coordination chemistry of azamacrocycles. The synthesis⁹⁴⁻⁹⁵ of ligands (Fig. 28,29 and Fig. 30) led to the study of their complexes. Studies on their complexes proved that all (Fig 28,29, and Fig. 30) form stable complexes with transition metal ions⁹⁶⁻⁹⁷ and the Cu²⁺ complex of the 14- membered

macrocycle shown in the (Fig. 29) is the most stable among these complexes.

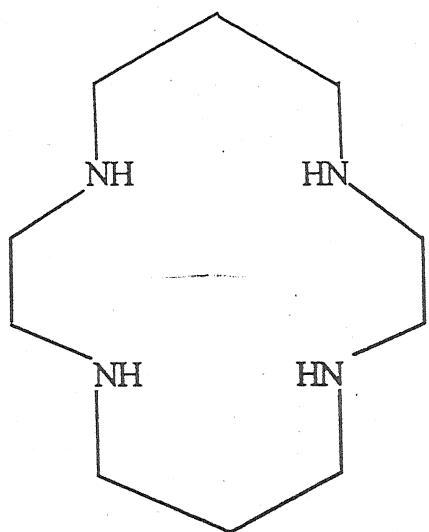


Fig. 27

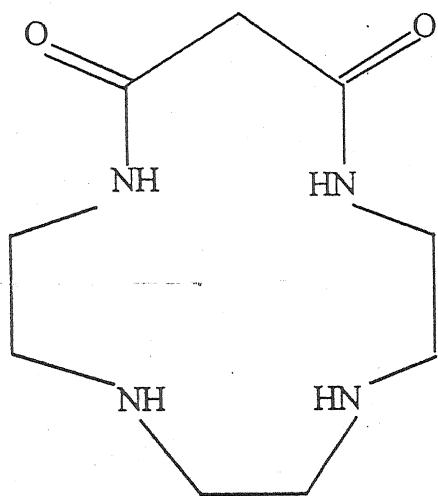


Fig. 28

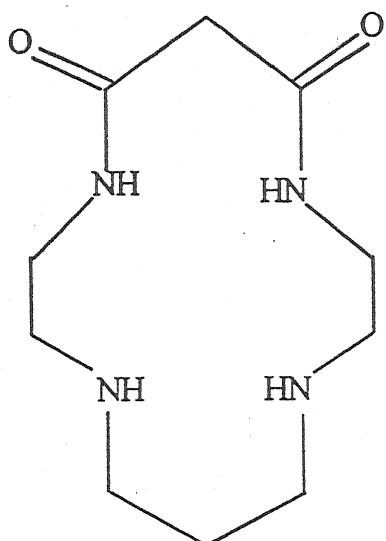


Fig. 29

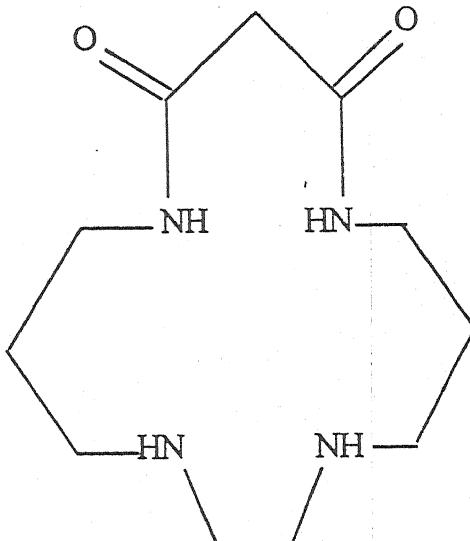


Fig. 30

Majority of nitrogen – donor macrocycles that have been studied are quadridentate ligands (Fig 31

and Fig. 32). To fully encircle a first row transition metal ion a macrocyclic ring size of between 13 and 16 members are required provided that the nitrogen donors are spaced such that five six or seven membered chelate rings are produced on coordination⁹⁸⁻⁹⁹. A number of larger ring macrocycles containing more than four donor atoms have also been reported and one example of such a large ring ligand¹⁰⁰ incorporating more than one metal ion is shown in (Fig.32.)

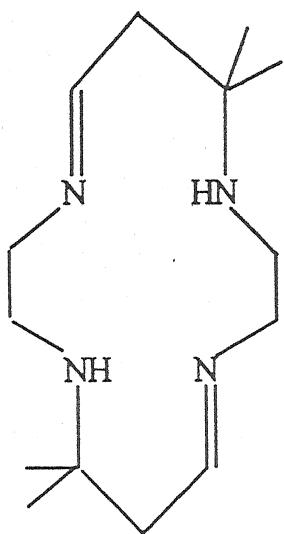


Fig 31

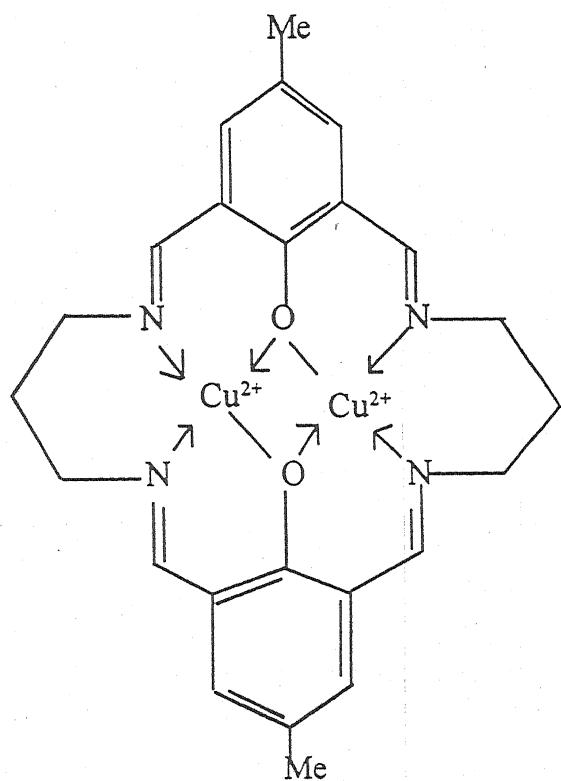
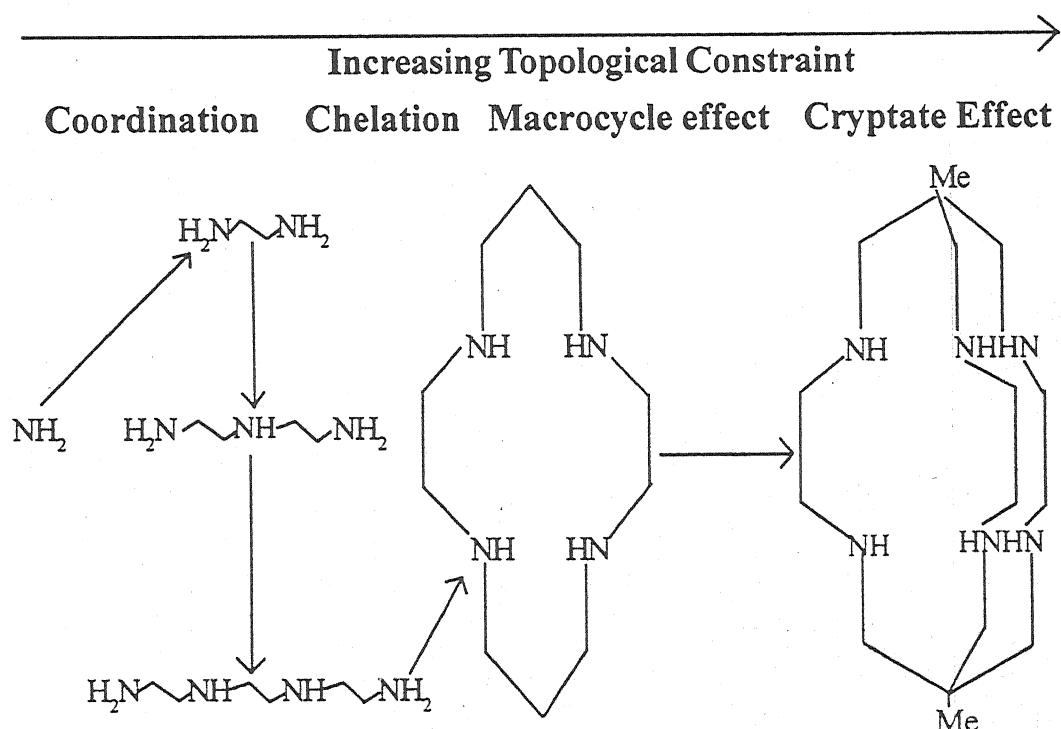


Fig 32

The enhanced stability of metal complexes of macrocyclic ligands over other linear polydentate ligands

is attributed to various structural effects namely, macrocyclic effect, chelate effect, cryptate effect and multiple juxtapositional fixedness (MJF)¹⁰¹ These effects which have been found to give stronger complexes arise from the structural factors, size, shape or geometry, connectedness or topology and rigidity of the macrocycle. (Fig. 33) displays the general observation that the affinity between ligands of a particular kind, amines in the example, and a given metal increases with the increasing topological constraint of the ligand system. This figure also illustrates (i) the chelate effect, which increases with the number of donors linked together through the series.



Topology and the Chelate, Macrocyclic and Cryptate Effect

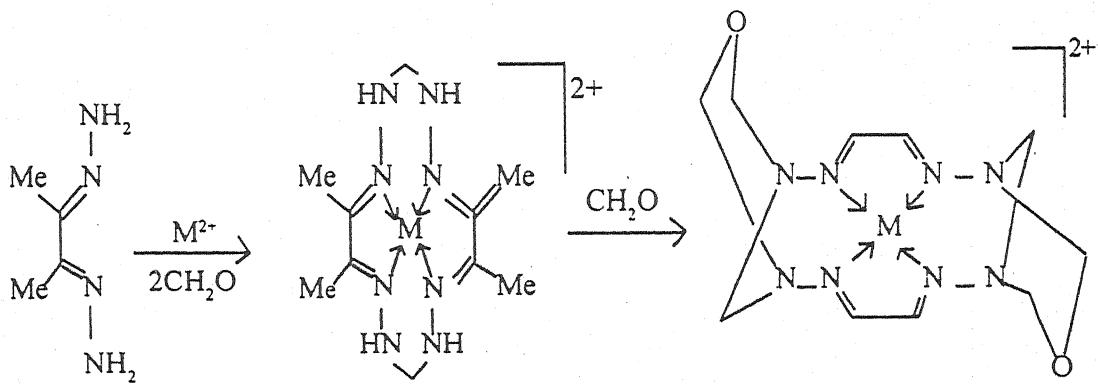
Fig. 33

- (i) ethylenediamine (en), diethylentriamine and N,N-bis (2-aminoethyl)-1,3 diaminopropane,
- (ii) the macrocyclic effect for the case of the tetra cyclotetradecane and the
- (iii) cryptate effect for the last structure.

The topological constraint is in the order, simple coordination < chelation < macrocyclic effect < cryptate effect. These topological effects are displayed in both kinetic and thermodynamic properties. This is manifested in equilibrium constants and is accompanied by exceptional kinetic inertness. **Cabbiness and Margerum** were the first to name the "macrocyclic effect" while reporting the first quantitative study of the relative thermodynamic and kinetic stability of tetra-aza macrocycles¹⁰²⁻¹⁰³. Subsequent studies on tetra-thia macrocycles¹⁰⁴, alkali metal complexes of crown ethers¹⁰⁵⁻¹⁰⁶ and various metal ion derivatives of cryptates¹⁰⁷ have confirmed the macrocyclic effect for macrocyclic ligands.

A variety of macrocyclic complexes which have adjacent nitrogen atoms (cyclic hydrazines, hydrazones or diazines) are formed by condensation reactions of hydrazine; substituted hydrazines or hydrazones with

carbonyl compounds. The reactions are parallel in diversity with those of amines, but are often more facile since the reacting NH_2 groups are not generally coordinated and the electrophile is thus not in competition with metal ion. The resulting macrocycles may be capable coordination isomerism, since either of the adjacent nitrogen atoms can acts as donor atom. Several macrocyclic ligands derived from hydrazine precursors have been reported¹⁰⁸⁻¹⁰⁹ and most of the studies involved in great deal with mononuclear complexes. However, less work has been reported for higher membered polyazamacrocyclic complexes. Goedken and Peng¹¹⁰ have reported the synthesis of the 14-membered octaazamacrocyclic complexes by the template condensation reaction of butane-2,3-dione dihydrazone with formaldehyde (Scheme 13).



Scheme 13

The amide macrocyclic ligands are of great interest because their metal complexes can function as porphyrin analogues in catalyzing organic oxidation reactions. The coordination chemistry of polyamide macrocycles is of particular interest in view of two potential donor atoms i.e., amide nitrogen and oxygen. However, in most of the polyamide macrocyclic complexes, amide nitrogen is engaged in coordination and not the oxygen. The formation of an amide is normally carried out after conversion of the carboxyl component to a more reactive acyl derivative which can react with the amino component under mild conditions. A number of macrocyclic tetraamides have been described in the literature. Rybka and Margerum have discussed the chemistry of a ligand (Fig. 34) which was prepared by the conventional methods employed in peptide synthesis. An American group has described a general method⁵⁷ for the synthesis of macrocyclic tetraamide ligands (Fig.35) by aminolysis of the thiazolidine-2-thione amides of dicarboxylic acids with diamines. Macroyclic tetraamides can be prepared in high yield by this route.

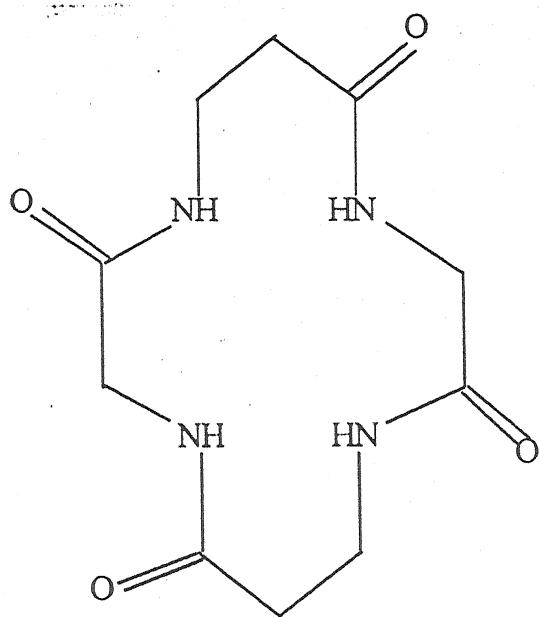


Fig. 34

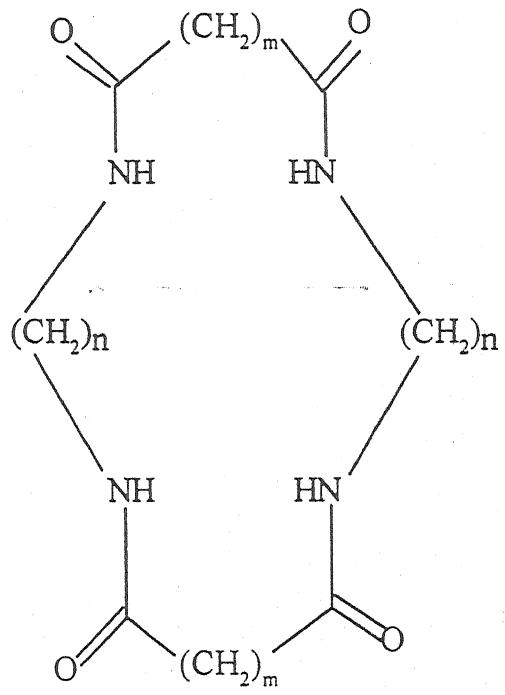


Fig. 35

In recent past Shakir and his co-workers¹¹¹⁻¹¹⁶ have developed a strategy for the synthesis of amide macrocyclic complexes. They have reported a wide variety of tetraaza, hexaaza and octaaza macrocyclic complexes bearing amide groups. Most of them were prepared via the template condensation reaction of "(2+2)" dicarboxylic acid with di or tri amines and self condensation of o-aminobenzoic acid. A series of reinforced macrocycles (Fig 36) has been reported.¹¹⁷ The first of this type of macrocycle was synthesized by Wlainright and Rama Subbu¹¹⁸⁻¹¹⁹ which showed much greater rigidity than do their non-reinforced analogues.

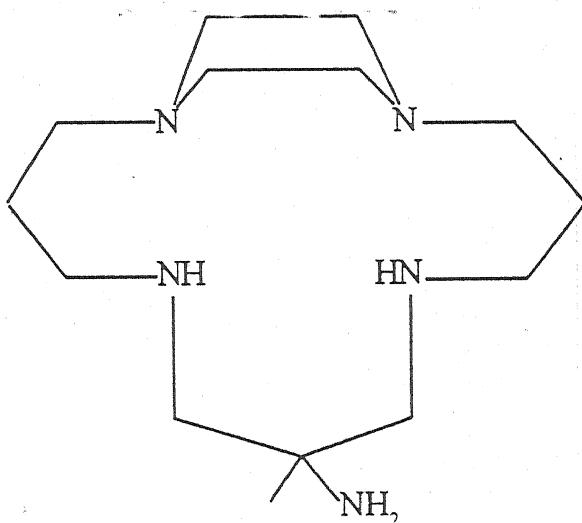


Fig. 36

The synthesis of the first cryptand (Fig. 37) in 1968 by Lehn and co-workers²⁸⁻²⁹, prompted the synthesis of

a large number of marcrobicycles and macropolycycles and studied their complexation properties.

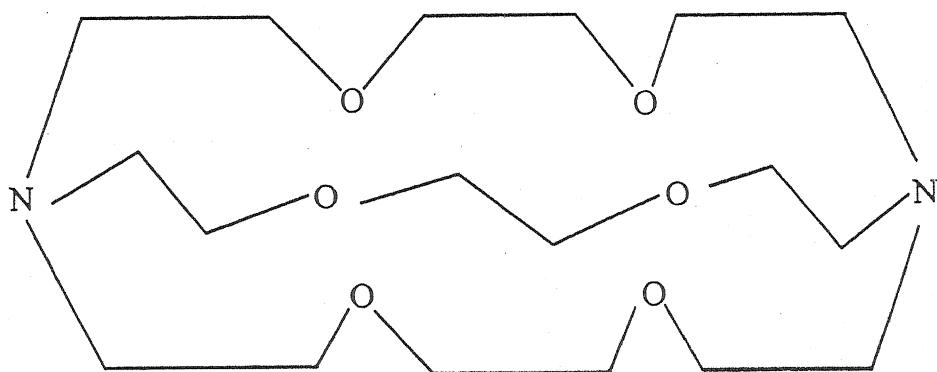


Fig . 37

A variety of binucleating macrocyclic ligands with similar and dissimilar coordination site have been reported and the later are of particular interest because such macrocyclic complexes are thermodynamically stabilized and kinetically retarded with regard to metal dissociation and metal substitution relative to metal complexes of acyclic ligand^{69,120}. Shakir and co-workers have reported¹²¹⁻¹²³ different series of binuclear macrocyclic complexes. Bis (macrocyclic) complexes incorporating two metal ions are of interest because they can act as multi-electron redox agents or catalysts and can be regarded as models for polynuclear metalloenzymes¹²⁴.

In recent years considerable attention has been devoted for the synthesis and characterization of mixed nitrogen, oxygen and sulfur donor atom macrocycles. L.f. Lindoy and associates¹²⁵⁻¹²⁶ synthesized novel macrocyclic ring (Fig.38) incorporating (O_4N_2 , $O_2S_2N_2$ and N_2S_4) donor set with emphasis on the recognition of ions with Co, Ni, Cu, Zn, Cd and Ag, Pb industrially important groups. Mixed donor macrocyclic ligands have proved to be especially suitable for use in studies of the above type since they do not tend to yield complexes exhibiting the very high kinetic and thermodynamic stabilities that are, for example, characteristic of macrocyclic ligand complexes containing a N_4 -donor set.

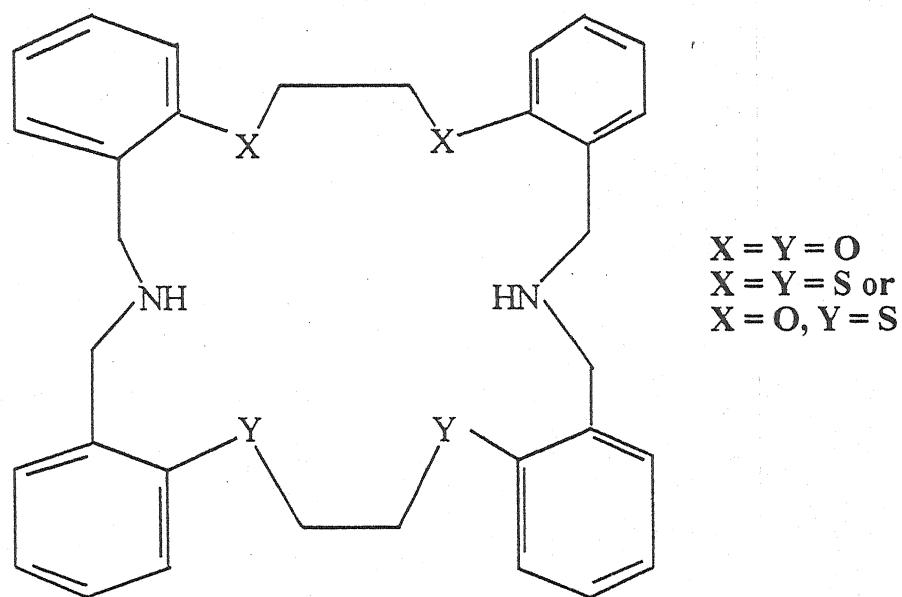


Fig. 38

Busch and Coworkers^{98,127} have synthesized several sulfur nitrogen containing macrocycles by in situ methods in presence of metal ions yielding the metal complex directly. Metal complexes mainly of nickel (II) and cobalt (II) containing two sulfur and two nitrogen donor^{8,128-130} four sulfur and four nitrogen donors¹³¹⁻¹³² two sulfur and four nitrogen and one sulfur and four nitrogen donors¹³³⁻¹³⁴ have been synthesized and in some cases the metal free ligand has also been obtained. The complexes with four sulfur and two nitrogen donors have four sulfur atoms in an equitorial plane and two nitrogen atoms are at trans positions. However, in two sulfur and four nitrogen donor atom complexes, the metal is located in a cavity bound by six donor atoms¹³⁵ octahedrally. **D.Funkemeier and his co-workers** have reported¹³⁶ the synthesis of 14-membered trans N₂S₂ dibenzo macrocycle (Fig. 39). **J. Scowen** with other researchers¹³⁷ reported metal ion directed synthesis of novel sulfur based (Fig. 40 and Fig. 41) macrocycles. Reaction forming acid stable dithiadiazia macrocycles proceeded in reasonable yield with carbon acid, even when stoichiometric amount of the carbon was employed. Evidently, the condensation reaction of forming 13 to 16 membered macrocycles for N₄ donor molecules transfers

readily to mixed S_2N_2 donor analogues with the presence of a pair cis disposed primary amine groups being the primary requirement for condensation.

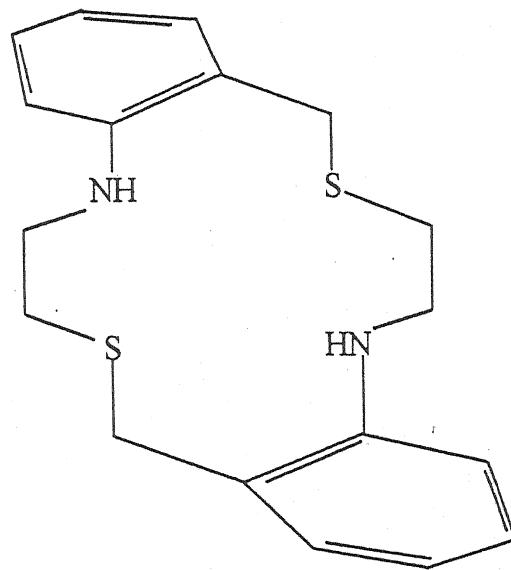


Fig 39

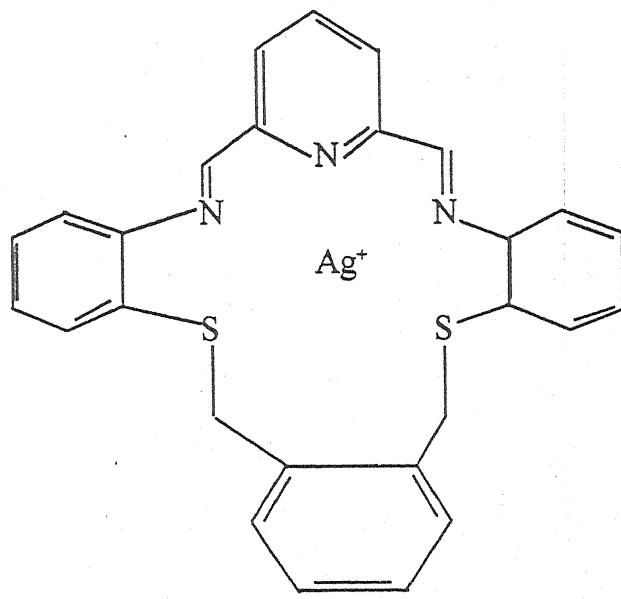


Fig 40

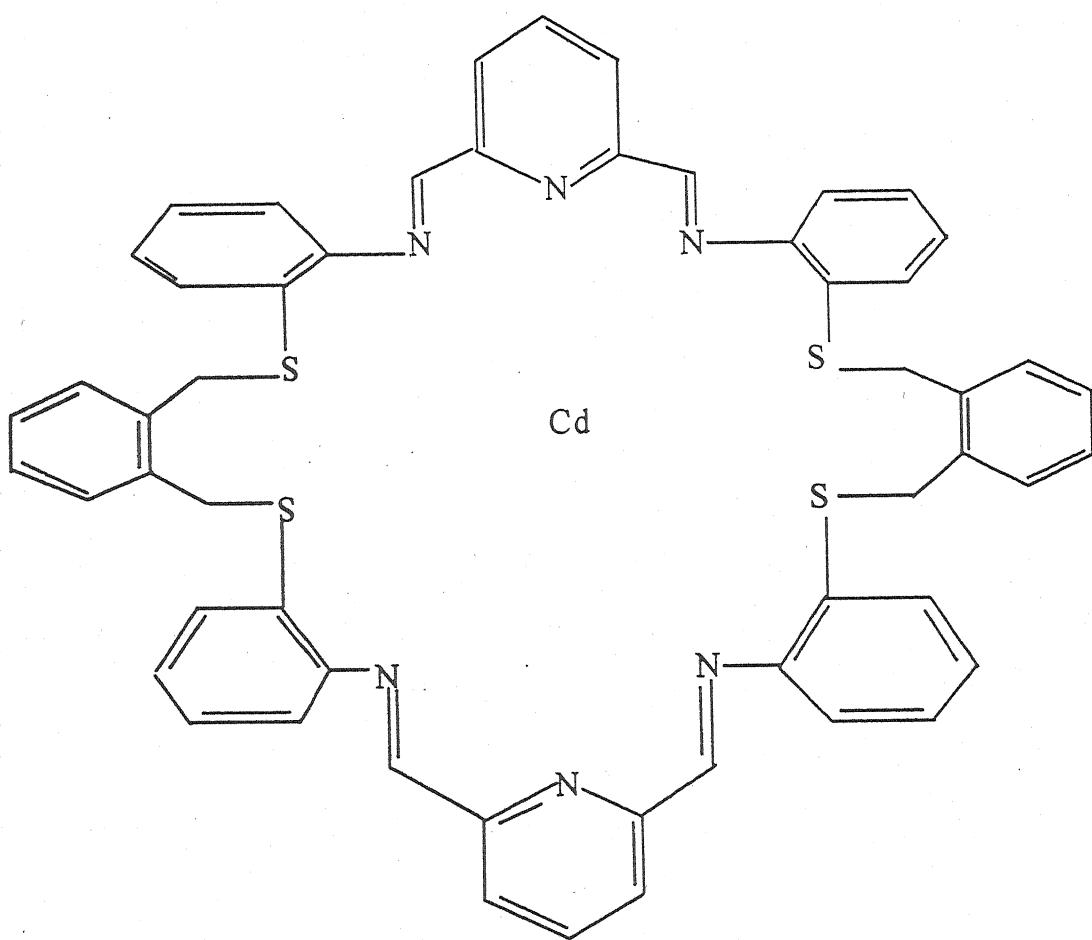


Fig . 41

Fenton and his coworkers¹³⁸⁻¹⁴⁰ have investigated the design and synthesis of oxaazamacrocyclic ligands with varying ring sizes and flexibilities including both weak and strong donor atoms in varied donor sets and sequences in order to define principles underlying transition metal

selectivity by macrocyclic ligands. Very recently Robertson¹⁴¹ and his coworkers have synthesized 20-membered N- benzylated macrocyclic ligands incorporating N₄O₂- donor sets, by performing macrocyclic ring closure using the appropriate N-benzylated triamine precursors by means of a Schiff base condensation with the corresponding dialdehyde, followed by *insitu* reduction of diamine linkages so formed. Much attention has been devoted in recent years for the development of macrocyclic complexes containing nitrogen sulfur or nitrogen, sulfur and oxygen donor atoms. Yasar Gok have recently synthesized¹⁴²⁻¹⁴³ 18-membered, dioxadithiadiazaza macrocycle 5,6 : 17,18-dibenzo - 11,12- (4- nitrobenzo)-2,3-bis(hydroxyimino)-7,16-dithia-10,13- dioxa- 1,4- diazacyclooctadecane and novel metal free phthalocyanies containing 12- membered diazadioxa macrocycles. Hokelek and his associates¹⁴⁴ have reported the crystal structue of 18-membered dioxo diaza dibenzo cyclooctadeca diene monohydrate ligand containing two ether oxygen and two aza nitrogen atoms.

The design of novel macrocyclic ligands and their complexes is interesting in view of their use as models to elaborate the metal ions interaction and to get an insight of

the coordinating sites in metalloproteins and in other biological systems¹⁴⁵⁻¹⁴⁷. These macrocyclic ligands also serve as models to study magnetic exchange phenomena. The macrocyclic ligands and their complexes have a diverse use in various fields. They are used as models for protein metal binding sites, pigments, vitamin B₁₂, photosynthesis, dioxygen, sodium and potassium ion transport¹⁴⁸⁻¹⁵⁰. In biomedical systems¹⁵¹⁻¹⁵⁹ they are used as therapeutic reagents¹⁶⁰⁻¹⁶⁴ in chelate therapy for the treatment of metal intoxication, as anti-HIV agents¹⁶⁵⁻¹⁶⁸ and as cyclic antibiotics whose antibiotic activity is because of specific metal complexation. Macroyclic complexes are also used as synthetic ionophores¹⁶⁹⁻¹⁷⁰ as sequestering reagent for specific metal ion¹⁷¹⁻¹⁷² as chemical sensors¹⁷³⁻¹⁸⁰ in catalysis. They have their rapidly growing applications as radiopharmaceuticals, contrast agents in magnetic resonance imaging¹⁸¹⁻¹⁸⁴ (MRI) and as luminescence sensors¹⁸⁵⁻¹⁸⁷. These areas have led to a considerable effort in developing reliable inexpensive synthetic routes for this category of compounds⁹⁻¹².

Thus, the macrocyclic chemistry is a rapidly emerging interdisciplinary field, bridging organic and inorganic

coordination chemistry which needs intensive research. In view of vast applications of macrocyclic ligands and their complexes it was thought worthwhile to carry out some synthesis of novel macrocyclic complexes which may add up to this vast area of knowledge.

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CHAPTER - II

Material & Techniques Used

This chapter deals with the source from where starting materials have been obtained. The details of analytical methods and various physicochemical techniques employed for the characterisation and elucidation of the structure of newly synthesised complexes are also given

Materials :

- (1) Solvents : E. Merck (L.R. grade) and Ranbaxy solvents were used after purification and drying by conventional methods
- (2) Mercuric : Aldrich (A.R. grade) were used Chloride
- (3) Mercuric : Aldrich (A.R. grade) were used Nitrate

Other starting materials used in the present investigation, prepared either from the reported method or obtained from commercial sources as listed in table 1 and were used after purification

Table 1 : Specifications

Sr. No.	Name	Source
1	3,4 - hexane dione	BDH
2.	1,3 - diamino propane	BDH
3.	1,4- diamino butane	BDH
4.	1,5- diamino pentane	BDH
5.	1,7 - diamino heptane	BDH
6.	1,8 - diamino octane	BDH
7.	1,9 - diamino nonane	BDH
8.	1,10 - diamino decane	BDH
9.	diethylene triamine	Aldrich
10.	benzaldehyde	BDH
11.	Salicylaldehyde	BDH
12.	Cyclohexanone	Aldrich
13.	Glutaric anhydride	Aldrich
14.	2, 6-diaminopyridine	Aldrich
15.	Semicarbazide hydrochloride	BDH
16.	Thiosemicarbazide	BDH
17.	2, 3- pentane dione	BDH
18.	Furil	Aldrich
19.	Benzoyl acetone	Aldrich
20.	Dibenzoyl methane	Aldrich

Experimental Techniques

The details of physicochemical techniques employed viz. melting point, conductance measurements, Infrared and X-ray photoelectron spectroscopy i.e. XPS for the characterisation and structural determination of the newly synthesised Hg(II) complexes are given below.

The melting point of the complexes were determined on electrically operated melting point apparatus (M/S/ Toshniwal) and the values reported are uncorrected.

The elemental analysis for C, H and N were determined on a semimicro scale at C.D.R.I. Lucknow.

Conductance of the complexes was measured at room temperature in DMF by Digisun Electronics conductivity Bridge.

The infrared spectra of the complexes and ligands were recorded on Perkin- Elmer 457 spectrometer at room temperature in CsI (for complexes) or in nujol (for ligands).

The X-ray photoelectron spectra i.e. XPS were recorded on a VG Scientific ESCA -3 MK II electron spectrometer. The Mgk_{α} X-Ray line (1253.6 eV) was used for photoexcitation. The $Cu 2p_{3/2}$ ($BE = 932.8 \pm 0.2$ eV) and $Au 4f_{7/2}$ ($BE = 83.8 \pm 0.1$ eV) lines were used for cross checking¹. All the spectra were recorded using the same spectrometer parameters of 50 eV pass energy and 4mm slit width. The reduced full width at half maximum (FWHM) at $Au 4f_{7/2}$ ($BE = 83.8$ eV) level under these conditions was 1.2 eV.

The powdered sample was mixed with high purity silver powder to reduce the charging effect. A thin layer of such a sample was pressed on a gold metal gauze which was welded to a nickel sample holder. The $Ag 3d_{5/2}$ level ($BE = 368.2$ eV) obtained from this sample was sharp and did not show any observable shift. Thus the charging of the sample if at all present was negligible¹. The spectra were recorded in triplicate in the region of interest.

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CHAPTER - III

Synthesis & Characterisation of the complexes

Introduction

The tetraazamacrocyclic ligands and their metal complexes have attracted growing interest among the coordination chemists followed by many workers on the metal controlled template synthesis of macrocyclic species^{1,2}. Tetraazamacrocycles, especially when coordinated to metal centers, are considered to be model for metalloporphyrins and metallocorins due to the presence of four nitrogen donor sites in a ring structure³⁻⁶. In these metal complexes the metal ions as well as the ring play important roles on different counts. The metal ion directs the reaction preferentially towards cyclic rather than oligomeric or polymeric products⁷. The use of metal as template in such reaction has led to the synthesis of many complexes of macrocyclic ligands⁸. Lindoy and coworkers⁹ have made elegant studies on ligand design and metal ion recognition of tetraaza and mixed polyaza macrocyclic complexes. Macroyclic ligands as well as their complexes have wide range of applications in the area like catalysis¹⁰⁻¹¹, dioxygen carriers¹²⁻¹³, as anticancer drugs¹⁴ and their use as radioimmunotherapeutic agents¹⁵. Many tetraazamacrocyclic complexes stabilize unusual oxidation

states of the metal species due to stabilization by back bonding between the metal and nitrogen¹⁶.

Condensation of primary diamine with haloalkanes has played a vital role in the development of synthetic macrocyclic ligands, which have been proved to be a fruitful source of tetraazamacrocycles. A literature search revealed¹⁷⁻²³ that a few number of tetraazamacrocyclic Hg(II) complexes have been prepared and characterized but no work has been done on Hg(II) complexes of macrocycles derived from 1,3-diaminopropane; 1,4-diaminobutane; 1,5-diaminopentane; 1,7-diaminoheptane; 1,8-diaminoctane; 1,9-diaminononane and 1,10-diaminodecane.

Experimental :

All solvents were reagent grade and purified as described else where prior to use [24]. HgCl_2 , $\text{Hg}(\text{NO}_3)_2$, 3,4-hexanedione, polyethylenediamines were purchased from Aldrich Chemical and used after purification [24].

Synthesis of the Tetraazamacrocyclic complexes

To ethanolic solution (20 ml) of HgX_2 ($\text{X}=\text{Cl}$,

NO_3) (1 mmol) a solution of 3,4- hexanedione (2 mmol) was added dropwise constant stirring. This was followed by dropwise addition of 1,3-diaminopropane (2 mmol) in ethanol (20 ml) with constant stirring for 5 hrs. A white solid appeared which was filtered, washed with ethanol and dried under vacuum over CaCl_2 . $[\text{HgL}^1\text{X}_2]$ (Scheme 1).

A similar procedure was adopted for the synthesis of Hg (II) complexes of macrocycles derived from 3,4-hexanedione with 1, 4-diaminobutane $[\text{HgL}^2\text{X}_2]$; 1, 5-diaminopentane $[\text{HgL}^3\text{X}_2]$; 1, 7-diaminoheptane $[\text{HgL}^4\text{X}_2]$; 1,8-diaminoctane $[\text{HgL}^5\text{X}_2]$; 1,9-diaminononane $[\text{HgL}^6\text{X}_2]$ and 1, 10-diaminodecane $[\text{HgL}^7\text{X}_2]$.

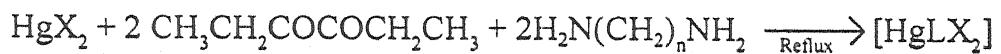
Characterization of the complexes :-

Elemental analyses were made by the microanalytical laboratory obtained from CDRI, Lucknow, India. Metals and chloride were determined volumetrically [25] and gravimetrically [26] respectively. The IR spectra ($4000-200\text{cm}^{-1}$) of all prepared complexes in CsI pellets were recorded with a Perkin-Elmer 621 spectrophotometer. The electrical conductivity of 10^{-3} M solution in DMF was

obtained with Digisum Electronic conductivity Bridge at room temperature. ^1H NMR spectra, recorded in DMSO-d6 using a Bruker AC 200 E spectrometer with Me_4Si as an internal standard, were obtained at the IIT Kanpur, India. The X-ray photoelectron spectra were recorded with a VG Scientific ESCA-3MK II electron spectrometer. The MgK_α X-ray line (1253.6 eV) was used for photo-excitation. The $\text{Cu } 2p_{3/2}$ ($\text{BE} = 932.8 \pm 0.2$) and $\text{Au } 4f_{7/2}$ ($\text{BE} = 83.8 \pm 0.1$) lines were used to calibrate the instrument and $\text{Ag } 3d_{5/2}$ ($\text{BE} = 368.2$) was used for cross checking [27]. All the spectra were recorded using the same spectrometer parameter of 50 eV pass energy and 4 mm slit width. The reduced full width at half maximum (FWHM) at the $\text{Au } 4f_{7/2}$ ($\text{BE} = 83.2$ eV) level under these conditions was 1.2 eV. The powdered sample was mixed with high purity silver powder to reduce the charging effect. A thin layer of such a sample was pressed on gold metal gauze, which was welded to a nickel sample holder. The $\text{Ag } 3d_{5/2}$ level ($\text{BE} = 368.2$ eV) obtained from this sample was sharp and did not show any observable shift. Thus, the charging of the sample, if at all present, was negligible [27]. The spectra were recorded in triplicate in the region of interest. In most cases the binding energies were reproducible within ± 0.1 eV.

The usual least-squares fitting procedure of determining peak positions, line widths and areas was used.

The complex may be synthesized by the following general method:



(Where X = Cl or NO₃; n = 3, 4, 5, 7, 8, 9, 10)

These synthesized complexes were white solid and stable at room temperature. All the complexes have shown high melting points > 225 °C. Elemental analyses were within ±0.5% for C, H, N, Hg and Cl. The molar conductance measurements of the complexes in DMF correspond to the non-electrolytic nature [28] (Table 1).

The preliminary characterization of the mercury containing macrocyclic complexes has been obtained from the IR spectra. The infrared spectra of the metal complexes show the absence of the stretching modes of functional groups (NH₂ and C=O), and the appearance of bands characteristic of the imines group [29-31]. The major changes observed in the spectra of the metal complexes are the absence of stretching and deformation vibrations

of NH_2 group, indicating their deprotonation and the appearance of strong bands due to coordinated $\nu(\text{C}=\text{N})$ vibrations in the range 1626-1605 cm^{-1} [29]. Strong and sharp band for C-H bending vibrations appears at ca.1460-1500 cm^{-1} [29]. The presence of the new bands in the spectra of the metal complexes in the region at 438-457 cm^{-1} due to $\nu(\text{Hg-N})$ vibration supports the coordination of the imines nitrogen to the mercury ion [32]. In the spectrum of the complexes the bands at 409, 413 and 1010-1040 and 1460-1550 cm^{-1} are observed, which may be assigned to coordinated chloro and nitrate group respectively [29-30].

^1H NMR spectrum of one representative Hg(II) complex (2) has been recorded. The α - CH_2 protons of the amine residue give a triplet δ -2.63 ppm due to coupling with the β - CH_2 protons. The β - CH_2 protons of the amine residue give a broad peak at δ -1.50 ppm. The remaining methylene protons (γ and others) of the amine residue give rise to a broad peak at δ -1.32 ppm. In macrocyclic precursor, 1,2,8,9-tetraphenyl-3, 7-diazaduohepta-2,7-diene-1, 9-dione (KIM, 3) the α - CH_2 protons have been reported to appear as a triplet at δ 3.63 ppm and β - CH_2 protons as a

quintet at δ 2.11 ppm [33].

The photoelectron peaks binding energies (BE) data of HgX_2 and $[\text{HgLX}_2]$ ($\text{Hg 4P}_{1/2}$) and N1s (where L=L¹, L², L³, L⁴, L⁵, L⁶, L⁷; X=Cl, NO₃) are listed in Table 2 (Fig. 1-5). It may be seen that Hg4P_{1/2} photoelectron binding energy values were observed to be higher in metal salts than in metal complexes (Fig.1), suggesting that the mercury ion have higher electron density in the metal complexes than the mercury salts due to involvement of the mercury ion in coordination [27]. Further, the N1s photoelectron peaks have a single symmetrical peaks with higher binding energy in $[\text{HgLCl}_2]$ complexes than free nitrogen atom N1s photoelectron, while N1s have shown two peaks with higher binding energy in $[\text{HgL(NO}_3)_2]$ complexes than free nitrogen atom, one for nitrogen coordinated from C=N group and other for nitrogen coordinated from NO₃ group (Table 2) [27] (Fig 1-5).

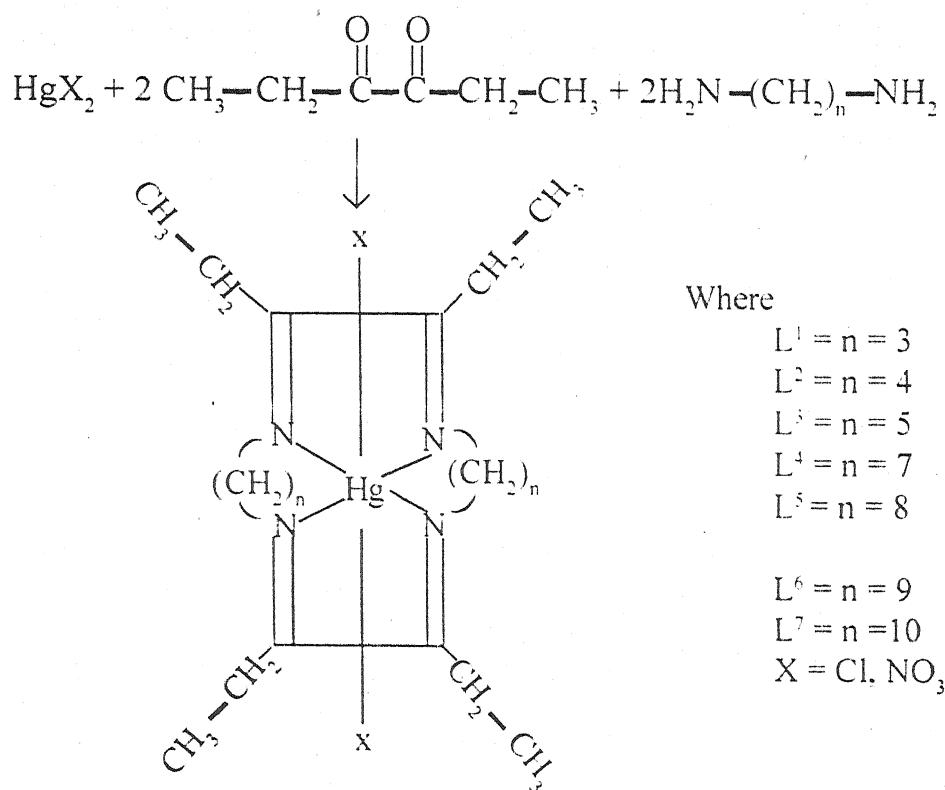
On the basis of elemental analysis, molar conductivity, IR and XPS data, the structure of these prepared complexes may be determined as shown in (fig. 1) and octahedral geometry may be established.

Table 1 - Elemental and Molar conductivity of $[\text{HgLX}_2]$ complexes where L=1, 2, 3, 4, 5, 6, 7; X = Cl, NO_3

Sr.NO	Compound	Found (Calcd)%			Molar conductivity ohm $^{-1}$ cm 2 mol $^{-1}$ (in DMF)
		C	H	N	
1.	$[\text{HgL}^1\text{Cl}_2]$	34.2 (34.5)	5.4 (5.5)	9.6 (9.7)	20
2.	$[\text{HgL}^2\text{Cl}_2]$	39.6 (39.7)	5.6 (5.9)	9.0 (9.2)	22
3.	$[\text{HgL}^3\text{Cl}_2]$	41.4 (41.7)	6.2 (6.3)	8.6 (8.8)	18
4.	$[\text{HgL}^4\text{Cl}_2]$	45.2 (45.3)	6.8 (6.9)	8.0 (8.1)	16
5.	$[\text{HgL}^5\text{Cl}_2]$	46.4 (46.9)	7.0 (7.2)	7.6 (7.8)	24
6.	$[\text{HgL}^6\text{Cl}_2]$	68.2 (48.4)	7.4 (7.5)	7.6 (7.5)	26
7.	$[\text{HgL}^7\text{Cl}_2]$	49.0 (49.4)	7.6 (7.7)	7.0 (7.2)	28
8.	$[\text{HgL}^1(\text{NO}_3)_2]$	34.0 (34.1)	5.0 (5.0)	13.2 (13.3)	16
9.	$[\text{HgL}^2(\text{NO}_3)_2]$	36.4 (36.5)	5.2 (5.4)	12.2 (12.4)	14
10.	$[\text{HgL}^3(\text{NO}_3)_2]$	38.6 (38.7)	5.6 (5.8)	12.0 (12.2)	20
11.	$[\text{HgL}^4(\text{NO}_3)_2]$	48.6 (48.7)	7.2 (7.4)	13.0 (13.1)	22
12.	$[\text{HgL}^5(\text{NO}_3)_2]$	43.2 (43.4)	6.6 (6.7)	10.2 (10.4)	18
13.	$[\text{HgL}^6(\text{NO}_3)_2]$	45.0 (45.1)	7.0 (7.1)	10.4 (10.5)	14
14.	$[\text{HgL}^7(\text{NO}_3)_2]$	46.4 (46.5)	7.0 (7.2)	10.0 (10.1)	12

**Table 2 : Binding energies (eV) in HgCl_2 ;
 $\text{Hg}(\text{NO}_3)_2$ and $[\text{HgLX}_2]$ (X=Cl,NO₃)
 Complexes**

Complexes	Metal Ion	Nitrogen N1s		Cl 2P
		Hg 4P _{1/2}	N	NO ₃
HgCl_2	79.4	-	-	202.8
HgCl_2L^1	678.4	403.8	-	203.8
HgCl_2L^2	678.4	403.8	-	203.8
HgCl_2L^3	678.4	403.8	-	203.8
HgCl_2L^4	678.4	403.8	-	203.8
HgCl_2L^5	678.4	403.8	-	203.8
HgCl_2L^6	678.4	403.8	-	203.8
HgCl_2L^7	678.4	403.8	-	203.8
$\text{Hg}(\text{NO}_3)_2$	679.8	-	404.6	-
$\text{Hg}(\text{NO}_3)_2\text{L}^1$	678.8	403.8	406.4	-
$\text{Hg}(\text{NO}_3)_2\text{L}^2$	678.8	403.8	406.4	-
$\text{Hg}(\text{NO}_3)_2\text{L}^3$	678.8	403.8	406.4	-
$\text{Hg}(\text{NO}_3)_2\text{L}^4$	678.8	403.8	406.4	-
$\text{Hg}(\text{NO}_3)_2\text{L}^5$	678.8	403.8	406.4	-
$\text{Hg}(\text{NO}_3)_2\text{L}^6$	678.8	403.8	406.4	-
$\text{Hg}(\text{NO}_3)_2\text{L}^7$	678.8	403.8	406.4	-



Where

$$L' = n = 3$$

$$L^2 = n = 4$$

$$L = n = 5$$

$$L = n = 5$$

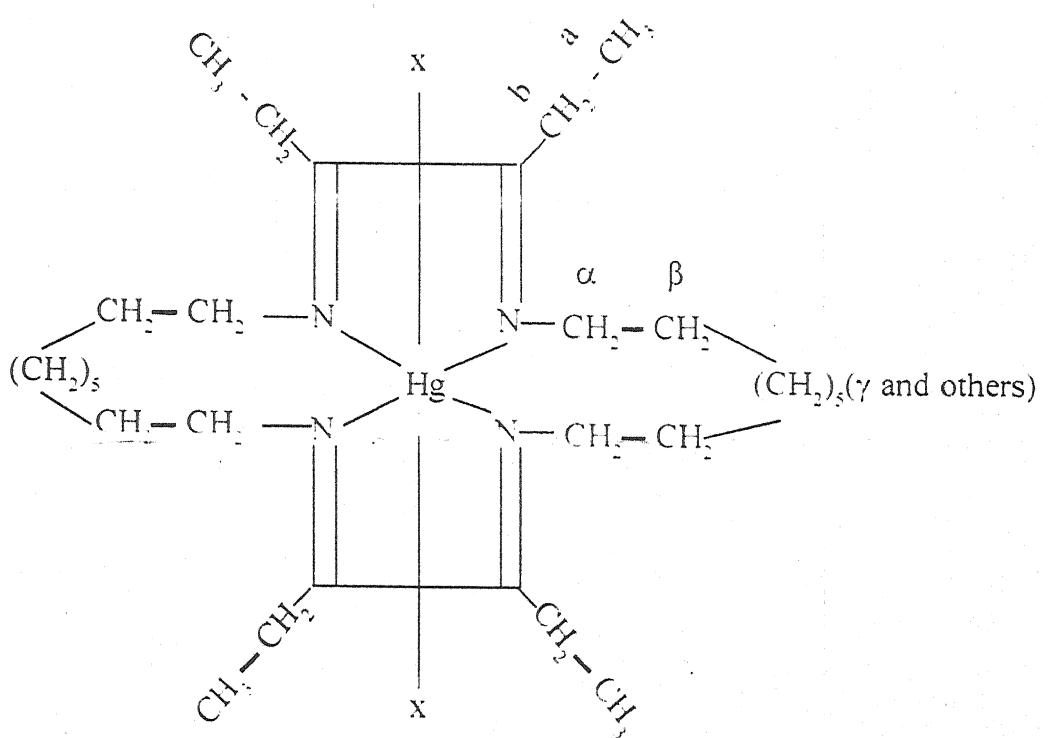
$$L^5 = n = 8$$

$$L^6 = n = 9$$

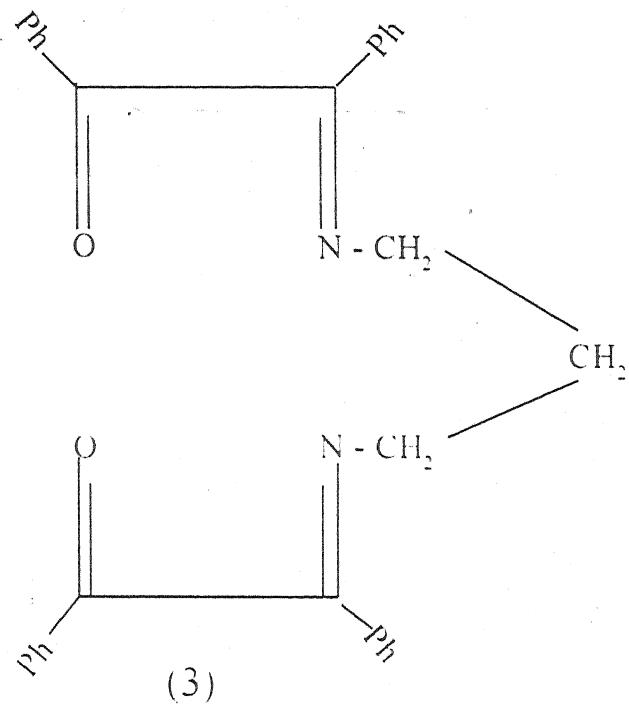
$$L^7 = n = 10$$

X = Cl, NO₂

Scheme 1. Synthesis of macrocyclic complexes



Structure of $[\text{HgX}_2\text{L}^6]$ Complex



1, 2, 8, 9 - tetraphenyl-3,7-diazaduo hepta -
2,7-diene - 1,9- dione (KIM)

Hg $4p_{1/2}$ photoelectron peak

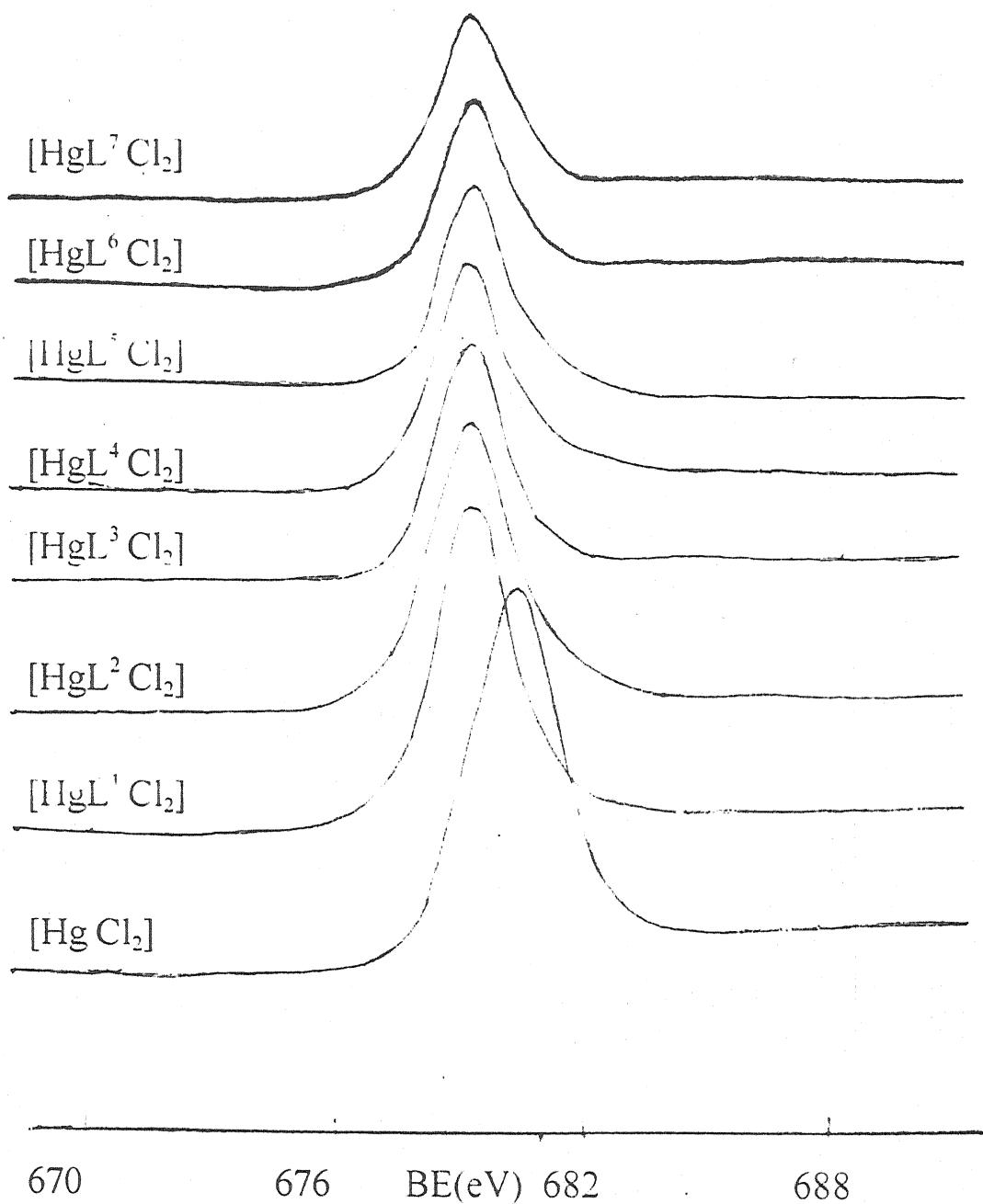


Fig 1 :- Hg $4p_{1/2}$ binding energies (eV) in HgCl_2 and $[\text{HgLCl}_2]$ complexes

Hg $4p_{1/2}$ photoelectron peak

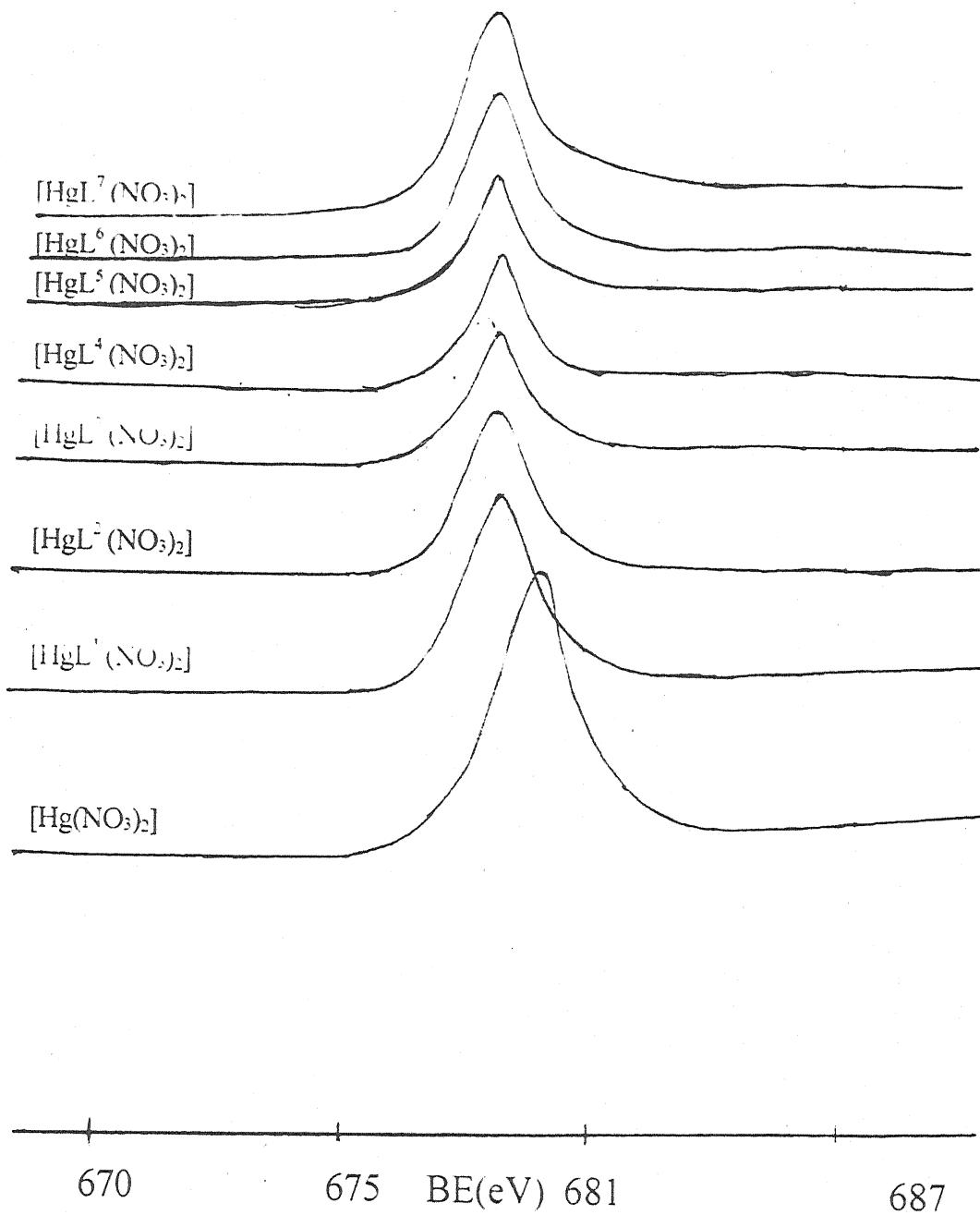


Fig 2 :- Hg $4p_{1/2}$ binding energies (eV) in $\text{Hg}(\text{NO}_3)_2$ and $[\text{HgL}(\text{NO}_3)_2]$ complexes

N1s photoelectron peak

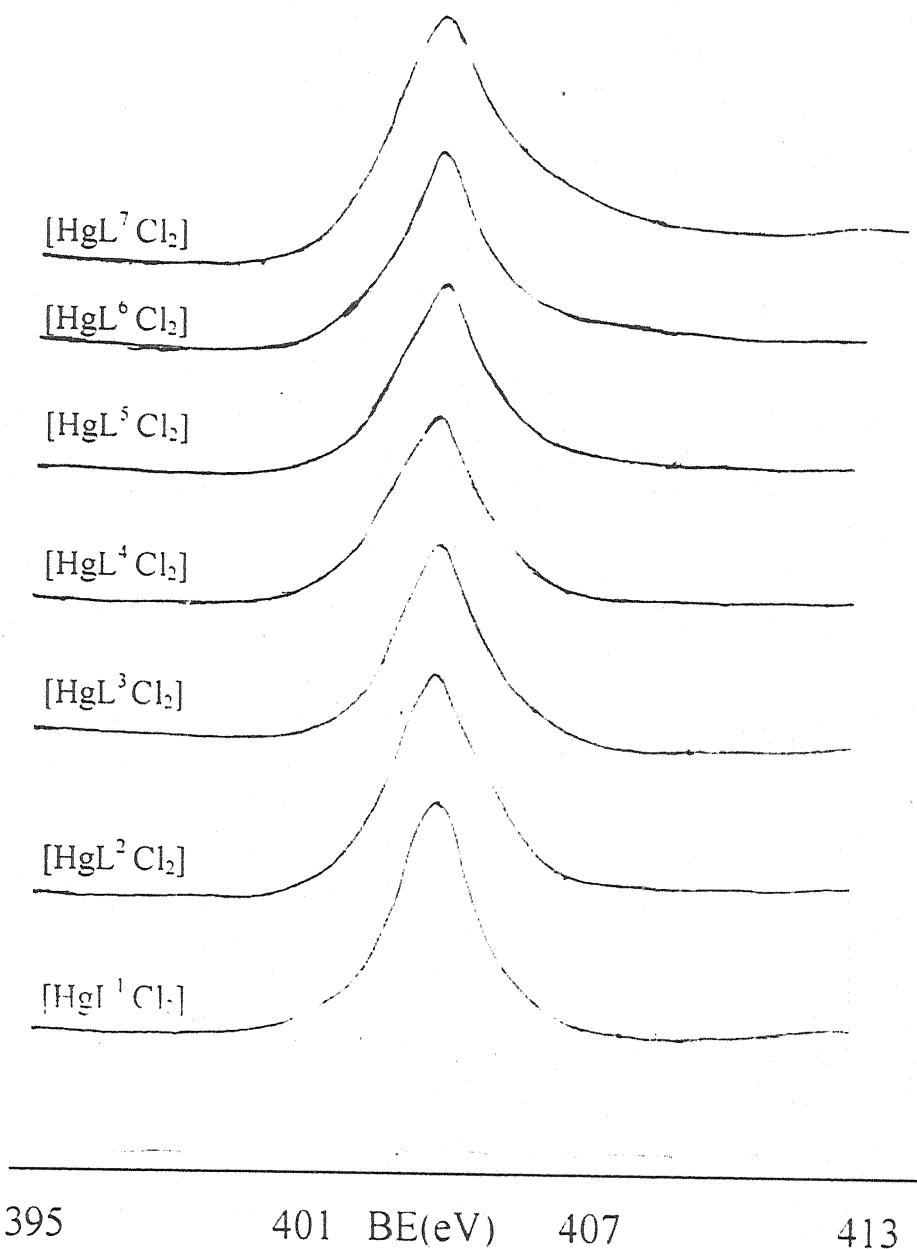


Fig3:- N1s binding energies (eV) in $[\text{HgLCl}_2]$
complexes

N1s photoelectron spectra

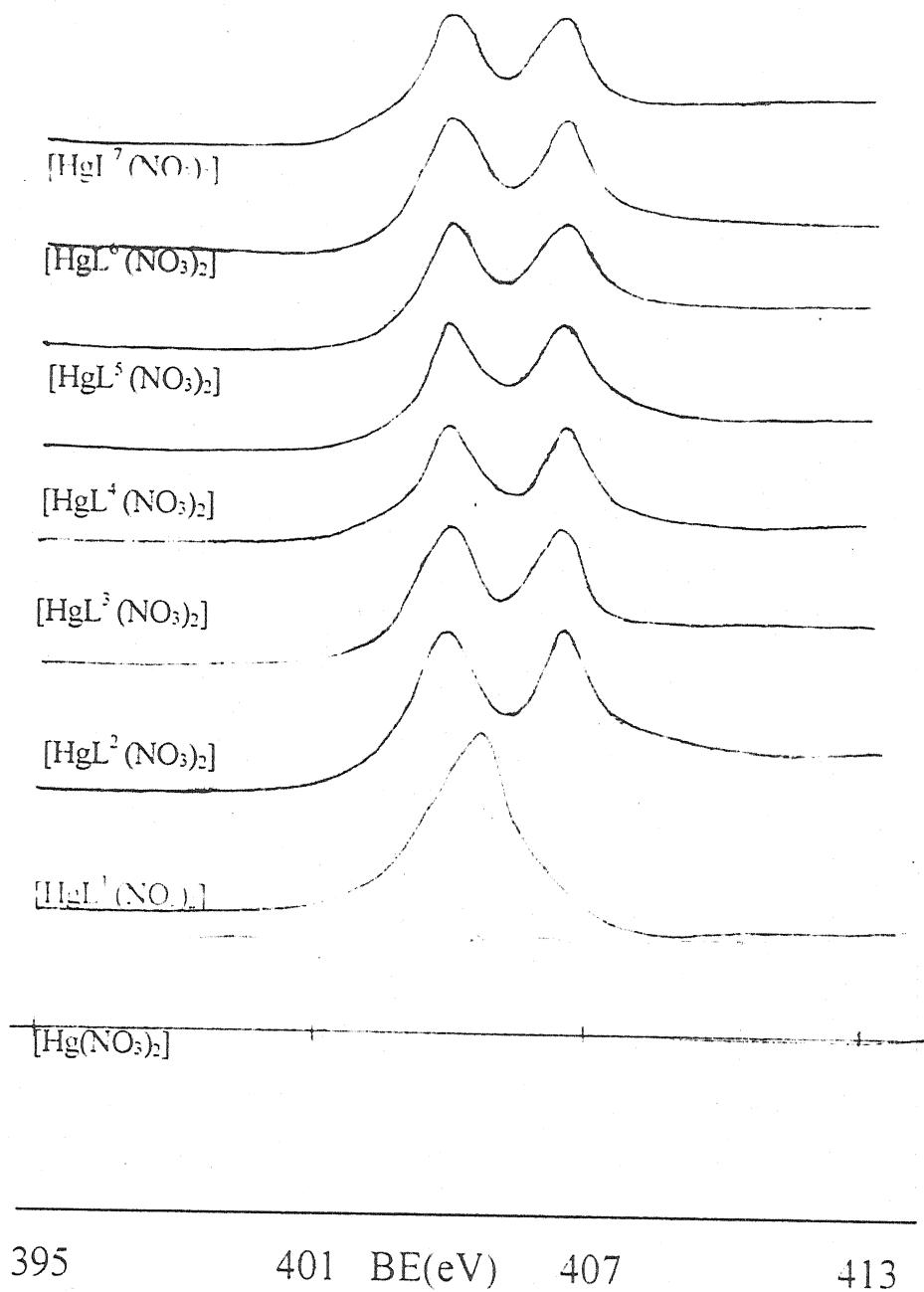
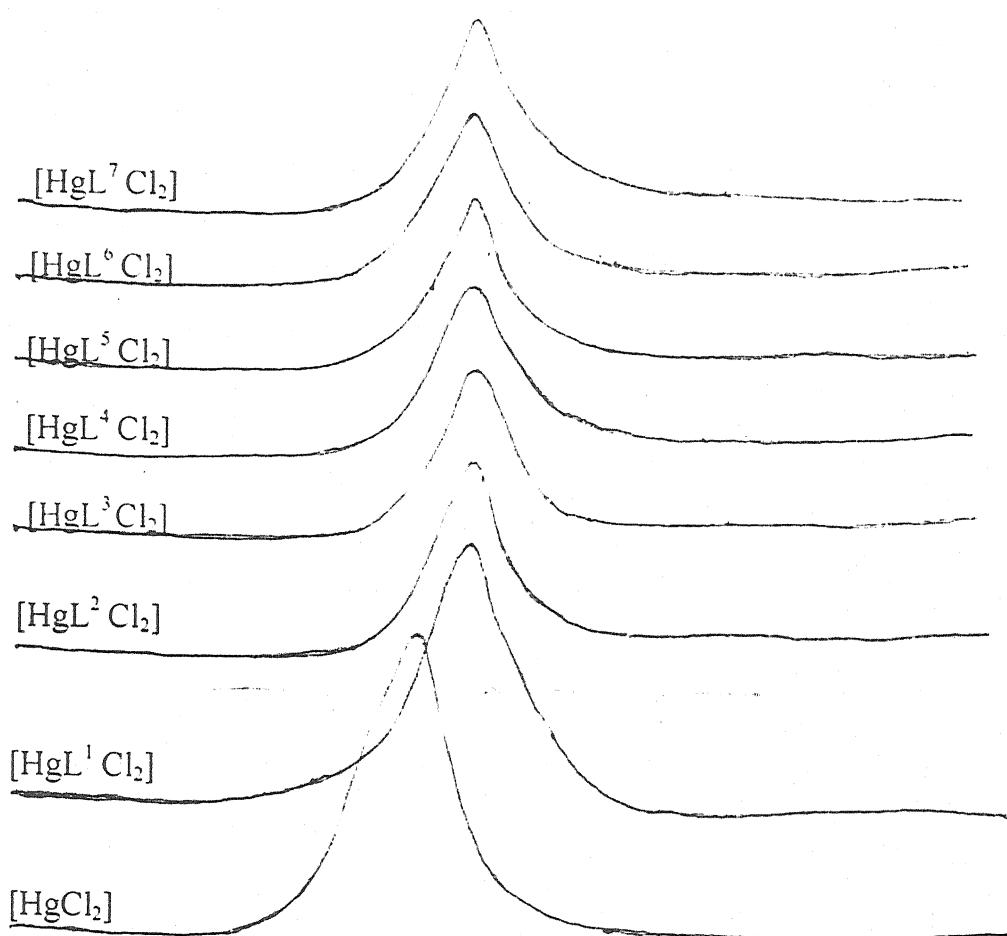


Fig 4 :- N1s binding energies (eV) in [HgL(No₃)₂] complexes

Cl 2p photoelectron spectra



195 201 BE(eV) 207 213

Fig 5 :- Cl 2p binding energies (eV) in $[\text{HgCl}_2]$ and $[\text{HgLCl}_2]$ complexes

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CHAPTER - IV

Synthesis and preparation of macrocyclic ligands

The tetraazamacrocyclic ligands and their metal complexes have attracted growing interest among coordination chemists followed by many workers on the metal controlled template synthesis of macrocyclic species [1, 2]. Tetraazamacrocycles, especially when coordinated to metal centre are considered to be model for metalloporphyrins and metallocorrins due to the presence of four nitrogen donor sites in a ring structure [3-6]. In these metal complexes the metal as well as the ring plays important roles on different counts. The metal ion directs the reaction preferentially towards cyclic rather than oligomeric or polymeric products [7]. The use of metal as template in such reactions has led to the synthesis of many complexes of macrocyclic ligands [8]. **Lindoy and coworkers** [9-11] have made elegant studies on ligand design and metal ion recognition of tetraaza and mixed polyaza macrocyclic complexes. Macroyclic ligands as well as their complexes have wide range of applications in the area like catalysis [10,11], dioxygen carriers [12-13], as anticancer drugs [14] and their use as radioimmunotherapeutic agents [15]. Many tetraazamacrocyclic complexes stabilize unusual oxidation states of the metal species due to stabilization by back bonding between metal and nitrogen [16].

A literature survey [17-23] revealed that very few tetraaza macrocyclic Hg (II) metal complexes have been prepared and characterized but no such work has been done on Hg(II) metal with macrocyclic ligands i.e. L^1 = 5,11-diethyl-6,12-dimethyl-3,8-dione-1,2,4,7,9,10-hexaazacyclododeca-1,4,6,10-tetraene; L^2 = 5,11-diethyl-6,12-dimethyl-3,8-dithione-1,2,4,7,9,10-hexaazacyclododeca-1,4,6,10-tetraene; L^3 = 5,6,11,12-tetrafuryl-3,8-dione-1,2,4,7,9,10-hexaazacyclododeca-1,4,6,10-tetraene; L^4 = 5,6,11,12-tetrafuryl-3,8-dithione-1,2,4,7,9,10-hexaazacyclododeca-1,4,6,10-tetraene; L^5 = 2,7,9,14-tetraphenyl-1,3,6,8,10,13-hexaazacyclooctadecane; L^6 = 2,7,9,14-tetrahydroxyphenyl-1,3,6,8,10,13-hexaazacyclooctadecane; L^7 = 2,7,9,14-tetracyclohexane-1,3,6,8,10,13-hexaazacyclooctadecane; L^8 = 23,24-Dioxo-1,6,9,12,17,20-hexaazacyclotetracosa-1,5,12,16-tetraene and L^9 = 25,26-Dioxo 1,6,12,17,23,24-hexaazacyclohexacosa-1,5,12,16-tetraene.

This chapter deals with the synthesis and characterization of Hg(II) metal complexes with such macrocyclic ligands.

All solvents were reagent grade and purified as

described elsewhere prior to use [16]. HgCl_2 , $\text{Hg}(\text{NO}_3)_2$, 2,3-pentanedione, semicarbazide, thiosemicarbazide, furil, diethylenetriamine, benzaldehyde, salicylaldehyde, cyclohexanone, glutaric anhydride, 2,6-diaminopyridine were purchased from Aldrich Chemical and used after purification [24].

Synthesis of Ligand (L^1 - L^2)

In an aqueous (50 ml) solution of semicarbazide hydrochloride (0.02 mol, 1.5g) or thiosemicarbazide (0.02mol, 1.8g) and 2,3-pentanedione (0.02mol, 2.08ml) were added slowly with constant stirring for 15-20 minutes. Both diamines and diketone were mixed in 1:1 molar concentration ratio. Mixture was cooled up to 5°C and kept undisturbed for 12 hrs. On cooling, white ppt. was formed. The precipitate was filtered, washed with distilled water and dried under vacuum over P_4O_{10} . The purity of the ligands was checked by TLC on silica -Gel G in DMSO Solution using anhydrous methanol 50% and THF 50% as eluent.

Synthesis of Ligand (L^3 - L^4)

Hot ethanolic solution (50 ml) of furil (0.02 mol, 3.82g) and hot aqueous solution (50 ml) of semicarbazide

(0.02mol, 0.7515 g) or thiosemicarbazide (0.02mol, 1.83 g) were added slowly with constant stirring. This mixture was refluxed at 80°C for 6-8 hrs. On cooling up to 5°C, cream colored precipitate was formed. The precipitate was filtered, washed with cold ethanol and dried under vacuum over P_4O_{10} . The purity of the ligands was checked by TLC on silica-GelG in DMSO solution using anhydrous methanol 50% and THF 50% as eluent.

Preparation of $[HgX_2L]$ Complexes (where $L = L^1$ to L^4).

HgX_2 ($X = Cl$ or NO_3), (1mmol) was dissolve in 20ml ethanol with constant stirring and 1 mmol of prepared macrocyclic ligand (L^1 or L^2 or L^3 or L^4) in 15 ml of ethanol was added. The stirring was continued for 5 hrs. The solid product was filtered, washed with ethanol and dried over vacuum. The purity of the complex was checked by TLC on silica-Gel G in DMSO solution using anhydrous methanol 50% and THF 50% as eluent.

Preparation of $[HgX_2L]$ Complexes (where $L = L^5$ to L^9).

All the complexes were prepared by template method.

Hot ethanolic solution (10 ml) of HgX_2 ($\text{X} = \text{Cl}$ or NO_3) (0.001 mol), hot ethanolic solution (10 ml) of diethylenetriamine (L^5 or L^6 or L^7 or L^8) (0.002 mol) and ethanolic solution of benzaldehyde or salicylaldehyde or cyclohexanone or glutaric anhydride (0.002 mol) are mixed together and the mixture is refluxed for 4-5 hrs. On cooling colored complexes precipitated out. These solid product was filtered, washed with ethanol and dried over P_4O_{10} under vacuum. The purity of complexes were checked by TLC on silica-Gel G in DMSO solution using anhydrous methanol 50% and THF 50% as eluent.

A hot ethanolic solution of glutaric anhydride (0.01 mol) is added to an ethanolic solution of 2,6-diaminopyridine (0.01 mol) L^9 and the resulting solution is refluxed for 1 hrs. A solution of HgX_2 ($\text{X} = \text{Cl}$ or NO_3) (0.005 mol) was then added to the above solution and refluxed for 4-6 hrs. On cooling the solution a crystalline compound separates out. It is then filtered, washed with ethanol and dried under vacuum over P_4O_{10} . The purity of the complex was checked by TLC on Silica-Gel G in DMSO solution using anhydrous methanol 50% and THF 50% as eluent.

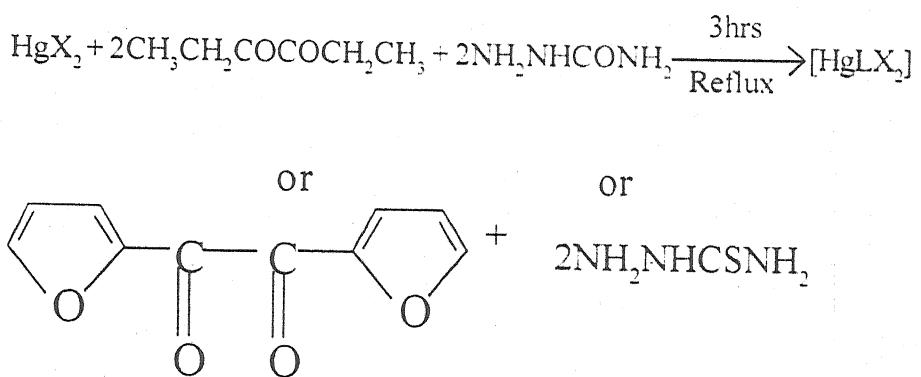


Characterization of the complexes -

Elemental analyses were made by the microanalytical laboratory obtained from CDRI, Lucknow, India. Metals and chloride were determined volumetrically [25] and gravimetrically [26] respectively. The IR spectra (4000-200 cm^{-1}) of all prepared complexes were recorded as CsI disc on a Perkin-Elmer 621 spectrophotometer. The electrical conductivity of 10^{-3} M solution in DMF was obtained on Digisum Electronic Conductivity Bridge at room temperature. The X-ray photoelectron spectra were recorded on a VG Scientific ESCA-3MK II electron spectrometer. The Mg $\text{K}\alpha$ X-ray line (1253.6 eV) was used for photo-excitation. The Cu $2p_{3/2}$ (BE=932.8 \pm 0.2) and Au $4f_{7/2}$ (BE = **83.8 \pm 0.1**) lines were used to calibrate the instrument and Ag $3d_{5/2}$ (BE = 368.2) was used for cross checking [27]. All the spectra were recorded using the same spectrometer parameter of 50 eV pass energy and 4 mm slit width. The reduced full width at half maximum (FWHM) at the Au $4f_{7/2}$ (BE = 83.2 eV) level under these conditions was 1.2 eV. The powdered sample was mixed with high purity silver powder to reduce the charging effect. A thin layer of such a sample was pressed on gold metal gauze, which was welded to a nickel sample holder. The

Ag $3d_{5/2}$ level (Eb 368.2 eV) obtained from this sample was sharp and did not show any observable shift. Thus, the charging of the sample, if at all present, was negligible [27]. The spectra were recorded in triplicate in the region of interest. In most cases the binding energies were reproducible within ± 0.1 eV. The usual least-squares fitting procedure of determining peak positions, line widths and areas was used.

The complex may be synthesized by the following general method :



(Where X = Cl or NO_3^-)

These synthesized complexes were white solid and stable at room temperature. All the complexes have shown high melting points. Elemental analyses were within $\pm 0.5\%$ for C,H,N, and Cl. The molar conductance measurements

of the complexes in DMF correspond to the non-electrolytic nature [28] (**Table 1**).

The infrared spectrum of ligand L^1 and L^3 does not exhibit any characteristics band for free - NH and - OH groups indicating the absence of free primary diamines and hydroxyl group, which suggest the complete condensation of keto group with amino group. In this spectrum, appearance of new bands characteristics of thioamide group at 1690 cm^{-1} ($\text{C}=\text{O}$) amide I, 1579 cm^{-1} (CO-NH), 1438 cm^{-1} (C-N) + $\delta(\text{N-H})$ amide II, 1262 cm^{-1} $\delta(\text{N-H})$ amide III and 728 cm^{-1} amide IV [29-31], which support the macrocyclic species. A sharp band observed in the region 3346 cm^{-1} and 3490 cm^{-1} may be assigned to $\nu(\text{N-H})$ of secondary amino group. IR spectra of all $[\text{HgX}_2\text{L}^1]$ and $[\text{HgX}_2\text{L}^3]$ complexes have shown the shifting in $\nu(\text{C}=\text{N})$, to the lower side than ligand and there is no change in $\nu(\text{C}=\text{O})$ and $\nu(\text{N-H})$ absorption bands in all $[\text{HgX}_2\text{L}^1]$ complexes than ligand, confirm that coordination takes place through the nitrogen of $\nu(\text{C}=\text{N})$ group, but not through $-\text{C}=\text{O}$ and $-\text{NH}$ groups.

The infrared spectrum of ligand L^2 and L^4 does not

exhibit any band around 3400 cm^{-1} characteristics for free-NH groups, indicating the absence of free primary amine and hydroxyl group, which suggest the complete condensation of keto group with amino group (32-33). In this spectrum, appearance of new bands characteristics of thioamide groups at $1607\text{ }\nu(\text{CN-NH})$, $1516\text{ }\nu(\text{C-N}) + \delta(\text{N-H})$, $1263\text{ }\delta(\text{N-H})$, which support the macrocyclic species. A broad band observed in the region 3168 cm^{-1} due to $\nu(\text{N-H})$ of secondary amino group. IR spectra of all $[\text{HgX}_2\text{L}^2]$ and $[\text{HgX}_2\text{L}^4]$ complexes have shown the shifting in $\nu(\text{C=N})$ to the lower side than ligand and there is no change in $\nu(\text{C=S})$ and $\nu(\text{N-H})$ absorption band in all $[\text{HgX}_2\text{L}^2]$ and $[\text{HgX}_2\text{L}^4]$ complexes than ligand, confirm that co-ordination takes place through the nitrogen of $\nu(\text{C=N})$ group, but not through $-\text{C=S}$ and $-\text{NH}$ groups.

An examination of the IR spectra of $[\text{HgX}_2\text{L}]$ (where $\text{L} = \text{L}^5, \text{L}^6, \text{L}^7, \text{L}^8$ & L^9) have shown the absence of absorption around 3400 cm^{-1} towards lower side in all there metal complexes indicates that coordination takes place thorough the nitrogen of the $\nu(\text{C=N})$ group.

IR spectra of $[\text{Hg}(\text{NO}_3)_2\text{L}]$ (where $\text{L} = \text{L}^5, \text{L}^6, \text{L}^7, \text{L}^8$ &

L^9) have shown absorption bands in the region 1420-1446, 1306-1320 and 1005-1020 cm^{-1} . This suggests that both nitrate groups are coordinated to the central metal ion as unidentate [34]. The IR spectra of $[\text{HgCl}_2L]$ (where $L = L^5$, L^6 , L^7 , L^8 & L^9) have shown absorption bands at 403-413 cm^{-1} , which are assigned as ν (Hg-Cl) group [35].

The $\text{Hg } 4p_{1/2}$ and $\text{N } 1s$ binding energies (eV) data of HgX_2 and $[\text{HgX}_2L]$ (where $X = \text{Cl}$ or NO_3 , $L = L^1, L^2, L^3, L^4$ & L^5, L^6, L^7, L^8, L^9) are listed in table 2. It may be seen that $\text{Hg } 4p_{1/2}$ photoelectron peaks binding energies values were observed more in metal salts than in metal complexes (table 1) (fig 1&2). It suggested that mercury ion have more electron density in metal complexes than metal salts due to involvement of metal ion in coordination [36]. Further, $\text{N } 1s$ have shown a single symmetrical peak with higher binding energy in $[\text{HgCl}_2L]$ complexes than free nitrogen atom $\text{N } 1s$ photoelectron peak or free ligand while $\text{N } 1s$ have shown two peaks with higher binding energy in $[\text{Hg}(\text{NO}_3)_2L]$ complexes than free nitrogen atom or free ligand; one for nitrogen coordinated $-\text{C}=\text{N}$ group, other nitrogen coordinated from $-\text{NO}_3$ group (table 1) [27] (fig 3 & 4). Furthermore $\text{Cl } 2p$ have shown higher binding

energies in $[\text{HgLCI}_2]$ complexes than $[\text{HgCl}_2]$; suggesting coordination of chlorine atom with mercury metal ion in these $[\text{HgLCI}_2]$ complexes (Fig. 7). S $2p$ photoelectron peak appeared on same position in $[\text{HgL}^2\text{X}_2]$ and $[\text{HgL}^4\text{X}_2]$ complexes as in ligand L^2 and L^4 , suggesting non involvement of sulphur atoms (Fig. 6).

On the basis of the above physico-chemical studies, a tentative structure and an octahedral geometry may be proposed, as shown in (fig 8-11).

Hg $4p_{1/2}$ photoelectron peak

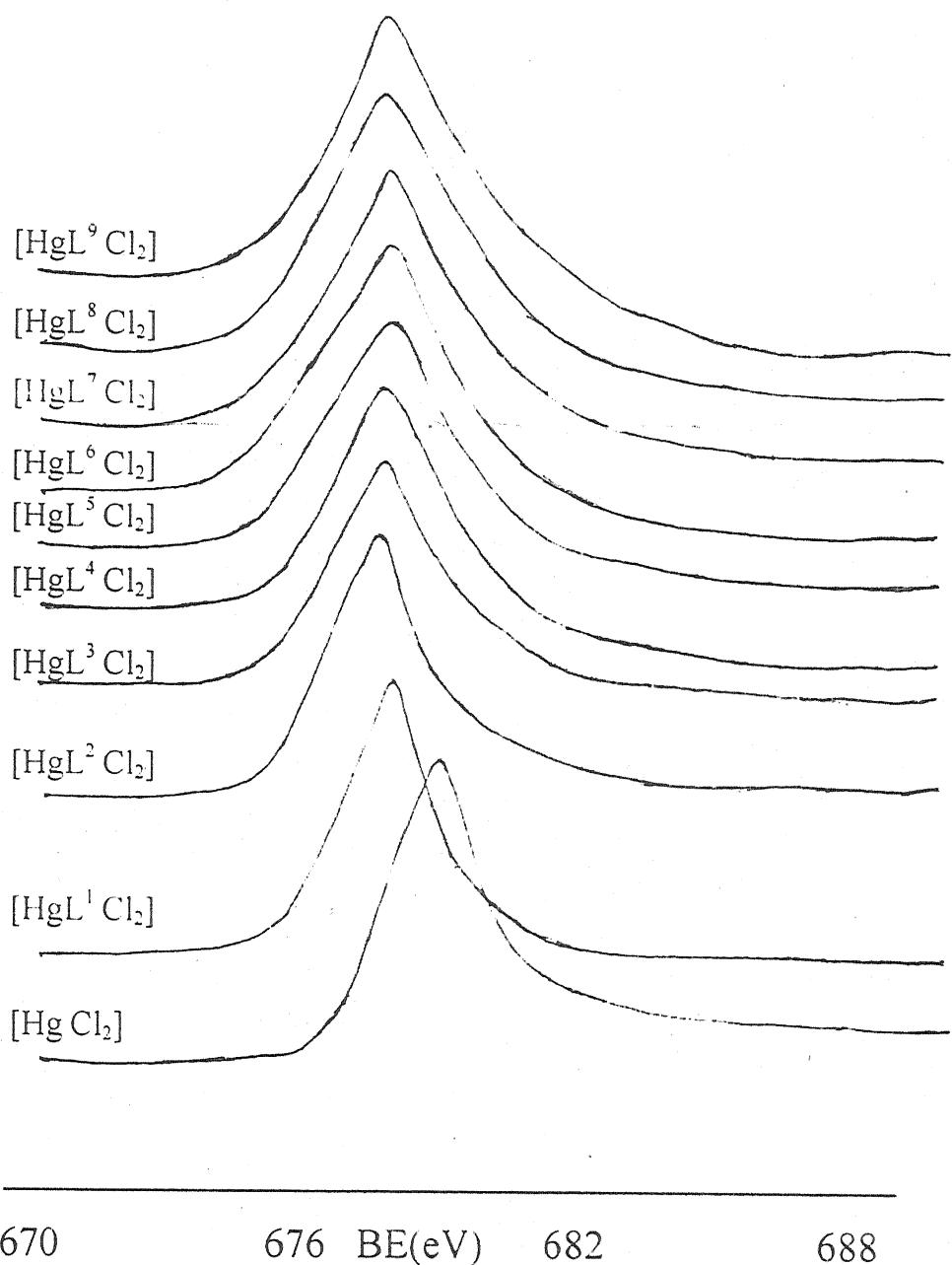


Fig 1 :- Hg $4p_{1/2}$ binding energies (eV) in $[HgCl_2]$
and $[HgLCl_2]$ complexes

Hg $4p_{1/2}$ photoelectron peak

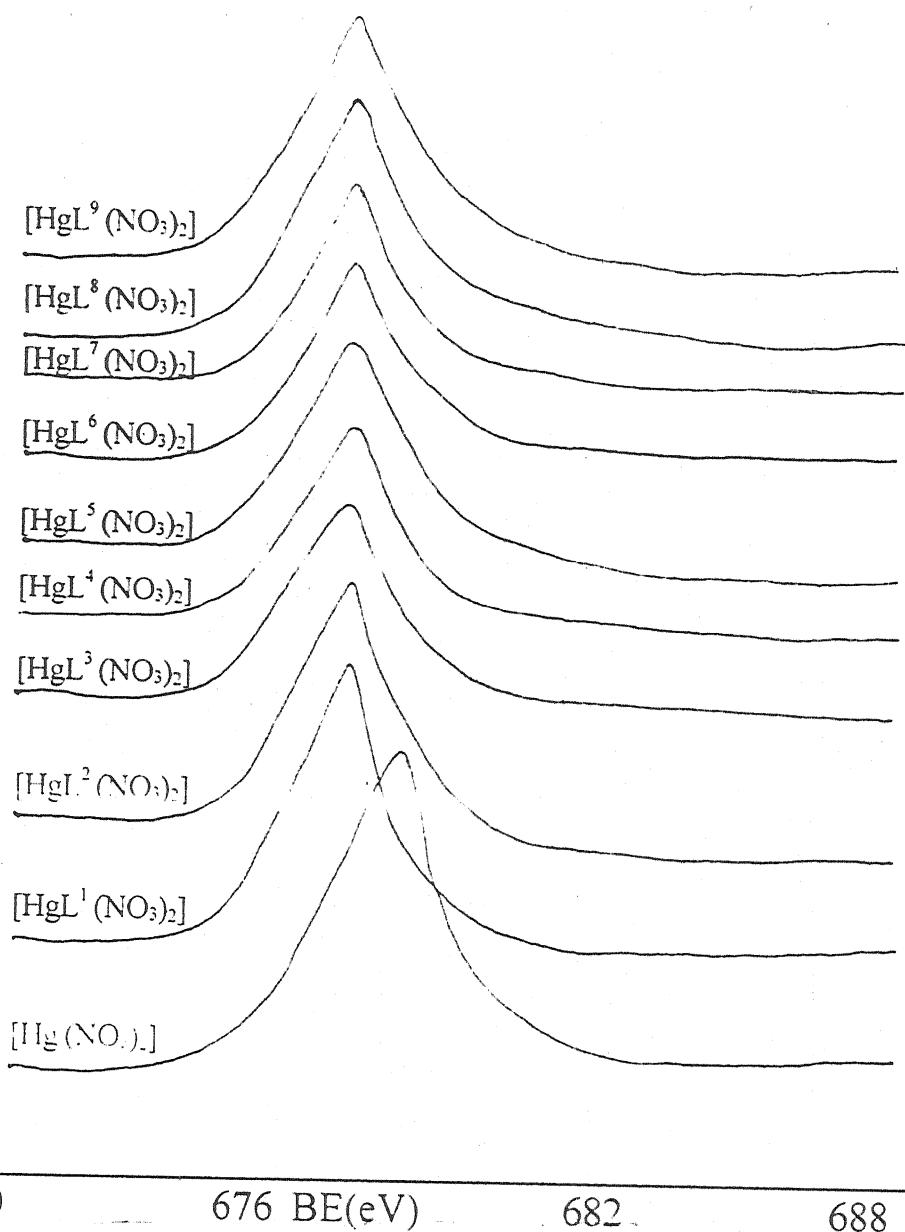


Fig 2 :- Hg $4p_{3/2}$ binding energies (eV) in $[\text{Hg}(\text{NO}_3)_2]$ and $[\text{HgL}(\text{NO}_3)_2]$ complexes

N1s photoelectron peak

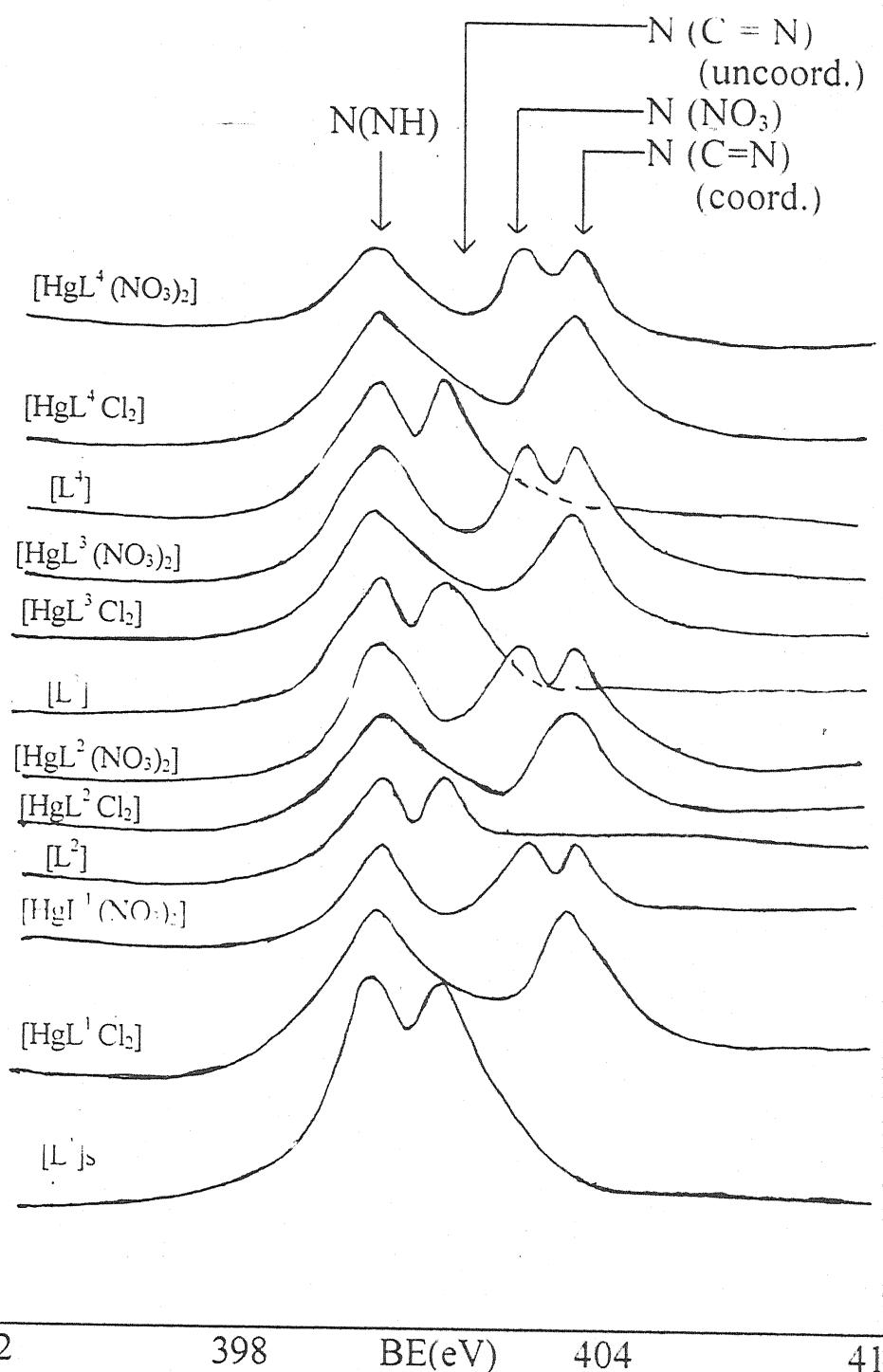


Fig 3 :- N1s binding energies (eV) in ligand and $[\text{HgLX}_2]$ complexes

N1s photoelectron peak

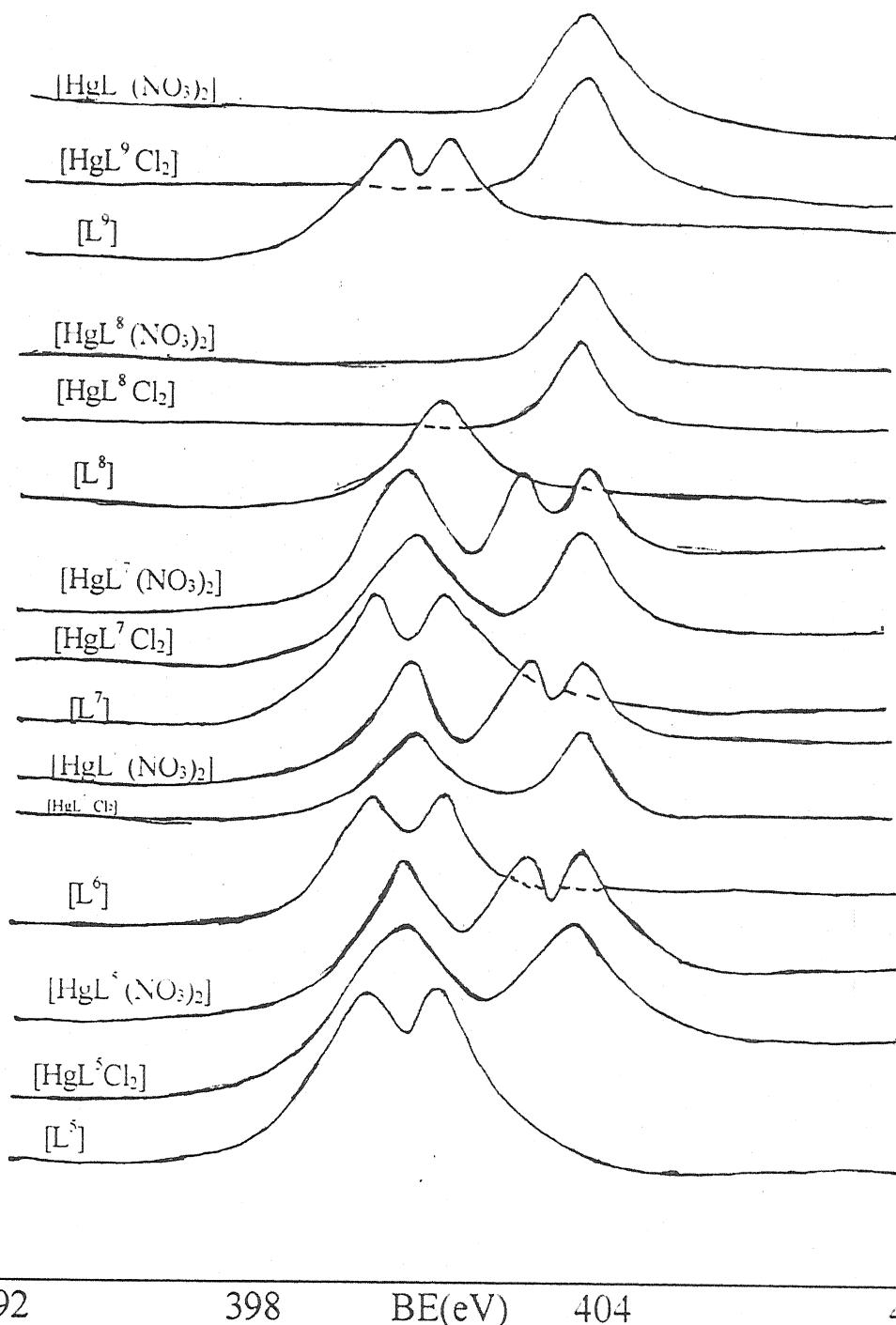
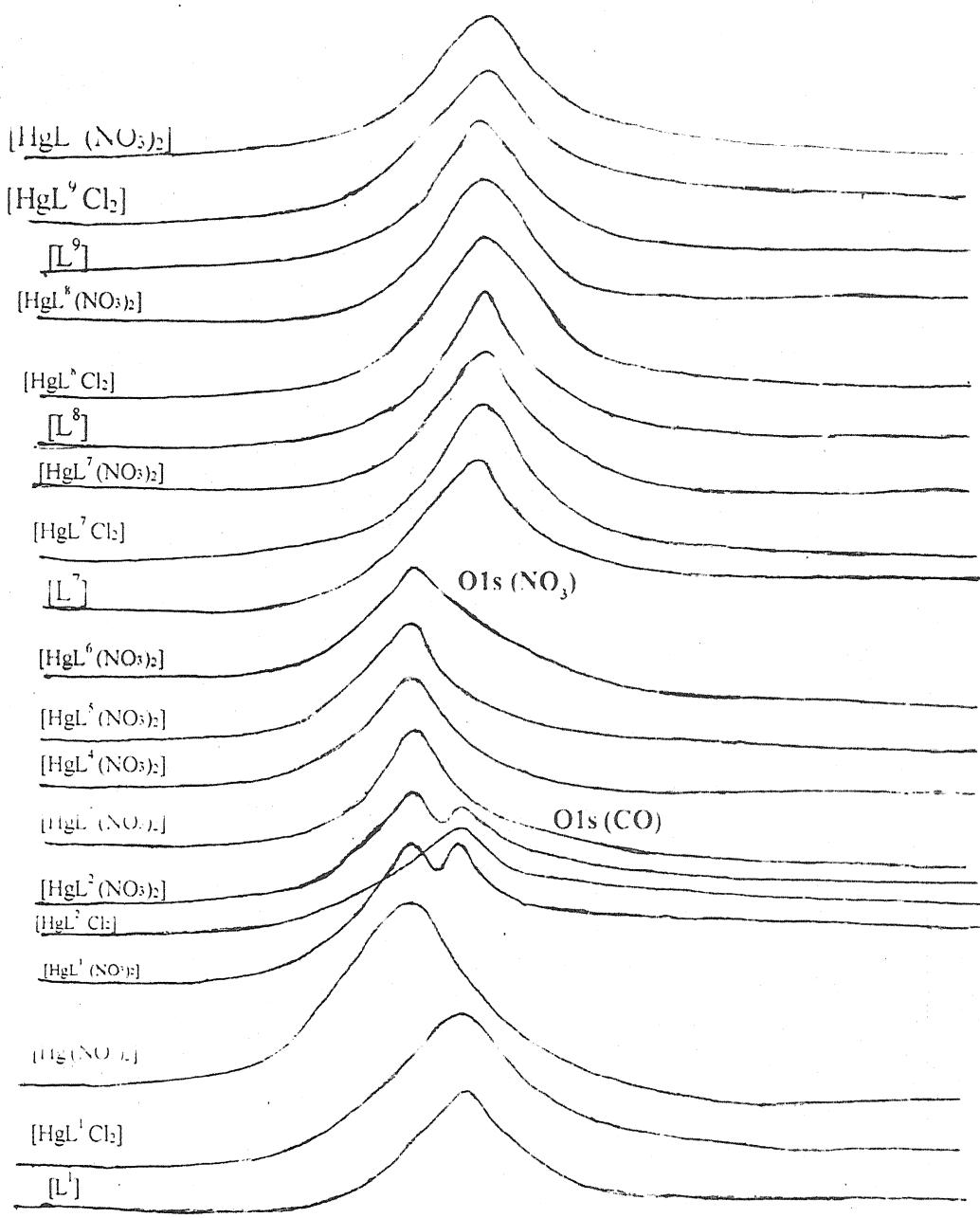


Fig 4 :- N1s binding energies (eV) in ligand and $[\text{HgLX}_2]$ complexes

O1s photoelectron peak

O1s (CO)



525 531 BE(eV) 537 543

Fig 5 :- O1s binding energies (eV) in ligand and
[HgLX₂] complexes

S 2p photoelectron peak

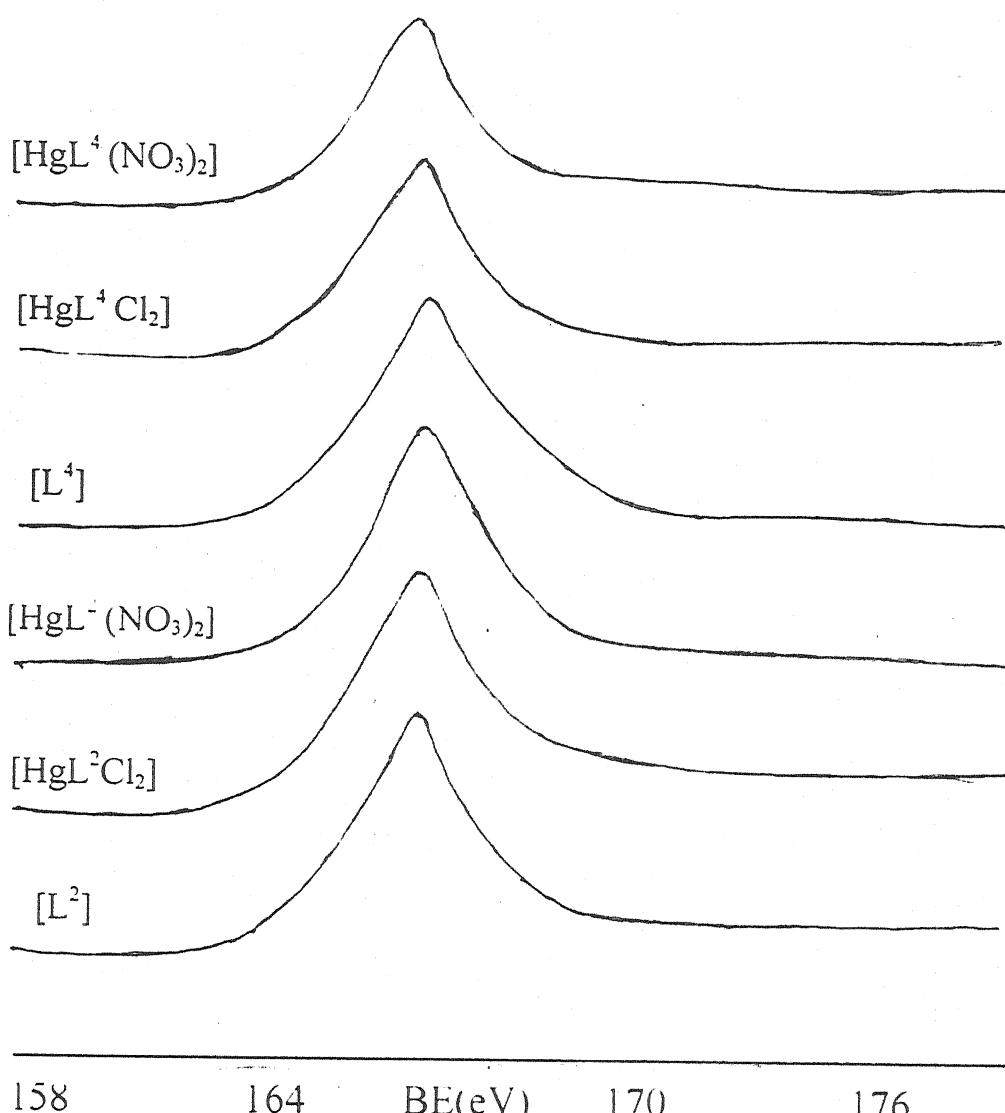


Fig 6 :- S 2p binding energies (eV) in L^2 , L^4 , $[\text{HgL}^2\text{X}_2]$ and $[\text{HgL}^4\text{X}_2]$ complexes

Cl 2p photoelectron peak

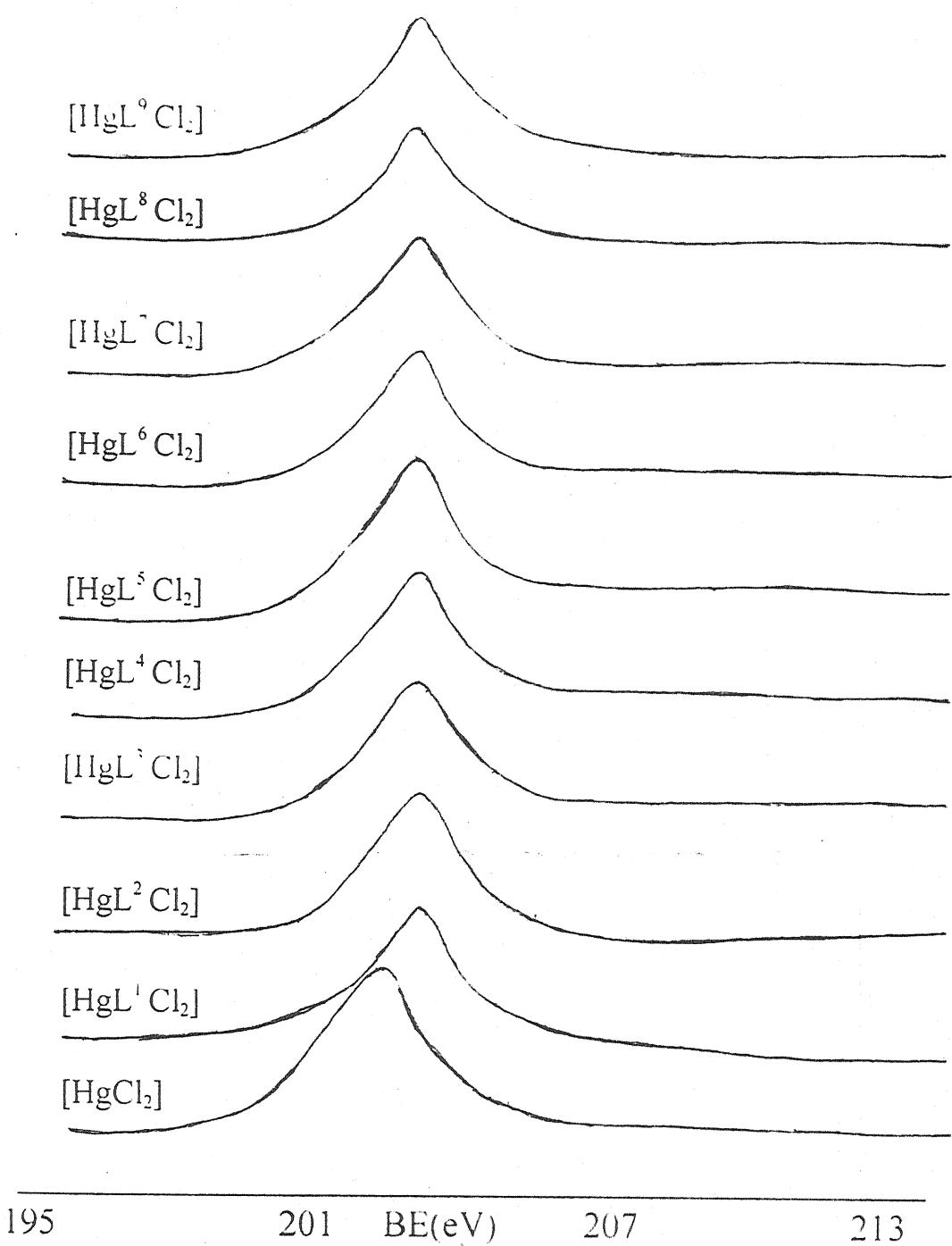


Fig 7 :- Cl 2p binding energies (eV) in $[\text{HgCl}_2]$ and $[\text{HgLCl}_2]$ complexes

Table 1 : Elemental and Molar conductivity of $[\text{HgLX}_2]$ complexes (where L = 1,2,3,4,5,6,7,8 & 9, X = Cl, NO_3)

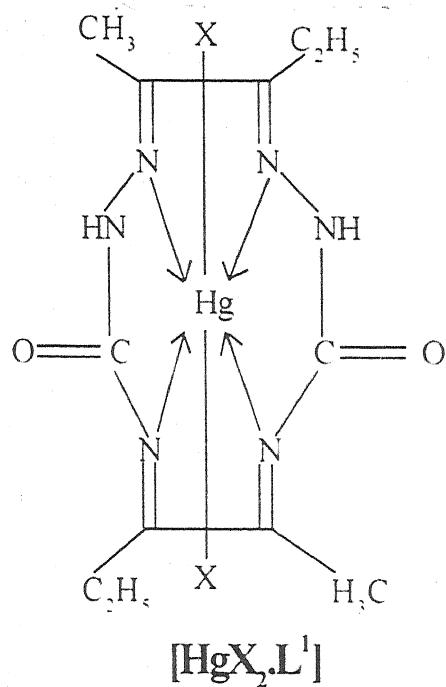
Sr.	Compound	Found (calcd)%			Molar Conductivity ohm ⁻¹ cm ² mol ⁻¹ in DMF
		C	H	N	
1	$[\text{HgL}^1\text{Cl}_2]$	26.0 (26.2)	3.0 (3.2)	15.0 (15.2)	10
2	$[\text{HgL}^1(\text{NO}_3)_2]$	23.63 (23.8)	2.8 (2.9)	18.4 (18.5)	15
3	$[\text{HgL}^2\text{Cl}_2]$	24.6 (23.7)	3.2 (3.0)	14.2 (14.4)	20
4	$[\text{HgL}^2(\text{NO}_3)_2]$	22.0 (22.1)	2.6 (2.7)	19.4 (19.6)	24
5	$[\text{HgL}^3\text{Cl}_2]$	36.0 (336.1)	1.8 (1.9)	11.4 (11.5)	22
6	$[\text{HgL}^3(\text{NO}_3)_2]$	33.6 (33.7)	1.6 (1.7)	14.2 (14.3)	18
7	$[\text{HgL}^4\text{Cl}_2]$	34.4 (34.6)	1.6 (1.8)	11.2 (11.0)	16
8	$[\text{HgL}^4(\text{NO}_3)_2]$	32.2 (32.4)	1.8 (1.7)	13.6 (13.7)	22
9	$[\text{HgL}^5\text{Cl}_2]$	52.0 (52.1)	4.6 (4.8)	10.0 (10.1)	24

10	[HgL ⁵ (NO ₃) ₂]	49.0 (49.0)	4.2 (4.5)	12.6 (12.7)	28
11	[HgL ⁶ Cl ₂]	47.6 (47.8)	5.4 (5.6)	9.2 (9.3)	16
12	[HgL ⁶ (NO ₃) ₂]	45.0 (45.2)	5.2 (5.3)	11.6 (11.7)	18
13	[HgL ⁷ Cl ₂]	48.0 (48.1)	7.0 (7.2)	10.4 (10.5)	20
14	[HgL ⁷ (NO ₃) ₂]	45.0 (45.1)	6.6 (6.8)	11.0 (11.2)	22
15	[HgL ⁸ Cl ₂]	31.6 (31.8)	3.6 (3.9)	13.8 (13.9)	16
16	[HgL ⁸ (NO ₃) ₂]	34.2 (34.4)	4.2 (4.3)	20.0 (20.1)	18
17	[HgL ⁹ Cl ₂]	34.6 (34.9)	2.0 (2.2)	13.4 (13.6)	20
18	[HgL ⁹ (NO ₃) ₂]	24.6 (24.8)	1.4 (1.6)	12.6 (12.8)	2

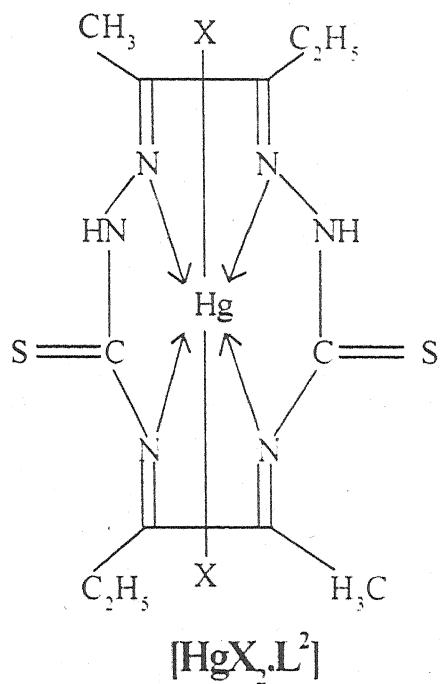
Table -2 Hg $4p_{1/2}$, N $1s$, S $2p$ and Cl $2p$ Binding energies (eV) in salt, ligands, $[\text{HgLCl}_2]$ and $[\text{HgL}(\text{NO}_3)_2]$ complexes.

Sr. No.	Salt, Ligand and Complex	Hg metal ion				N $1s$				O $1s$				S $2p$		Cl $2p$	
		Hg $4p_{1/2}$	Hg $4p_{3/2}$	N $_{(\text{NH})}$	N $_{(\text{NO}_3)}$	N $_{(\text{Py})}$	N $_{(\text{C}=\text{N})}$	O $_{(\text{NO}_3)}$	O $_{(\text{O})}$	O $_{(\text{C}=\text{O})}$	O $_{(\text{O})}$	O $_{(\text{C}=\text{O})}$	O $_{(\text{O})}$				
1	HgCl_2	678.8	572.8	-	-	-	-	-	-	-	-	-	-			201.2	
2	$\text{Hg}(\text{NO}_3)_2$	678.6	572.6	-	400.2	-	-	532.2	-	-	-	-	-				
3	L^1	-	-	399.4	-	400.8	-	-	-	533.2	-	-	-				
4	$[\text{HgL}^1\text{Cl}_2]$	677.8	571.8	399.4	-	403.8	-	-	-	533.2	-	-	-	202.2			
5	$[\text{HgL}^1(\text{NO}_3)_2]$	677.6	571.6	399.4	402.8	403.8	532.2	-	533.2	-	-	-	-				
6	L^2	-	-	399.4	-	400.8	-	-	-	-	-	-	-	166.4			
7	$[\text{HgL}^2\text{Cl}_2]$	677.6	571.6	399.4	-	403.8	-	-	-	-	-	-	-	166.4		202.2	
8	$\text{HgL}^1(\text{NO}_3)_2$	677.4	571.4	399.4	402.8	403.8	532.2	-	-	-	-	-	-	166.4			
9	L^3	-	-	399.4	-	400.8	-	-	-	-	-	-	-				
10	$[\text{HgL}^3\text{Cl}_2]$	677.8	571.8	399.4	-	403.8	-	-	-	533.2	-	-	-				
11	$\text{HgL}^3(\text{NO}_3)_2$	677.6	571.6	399.4	402.8	403.8	532.2	-	533.2	-	-	-	-				
12	L^4	-	-	399.4	-	400.8	-	-	-	-	-	-	-	166.4			
13	$[\text{HgL}^4\text{Cl}_2]$	677.6	571.6	399.4	-	403.8	-	-	-	-	-	-	-	166.4		202.4	
14	$\text{HgL}^4(\text{NO}_3)_2$	677.6	571.6	399.4	402.8	403.8	532.2	-	-	-	-	-	-	166.4			
15	L^5	-	-	399.4	-	400.8	-	-	-	-	-	-	-				
16	$[\text{HgL}^5\text{Cl}_2]$	677.8	571.6	401.2	-	403.8	-	-	-	-	-	-	-	202.4			
17	$\text{HgL}^5(\text{NO}_3)_2$	677.6	571.6	401.2	402.8	403.8	532.2	-	-	-	-	-	-				
18	L^6	-	-	399.4	-	400.8	-	-	-	-	-	-	-				
19	$[\text{HgL}^6\text{Cl}_2]$	677.8	571.6	401.4	-	403.8	-	-	-	-	-	-	-	202.4			

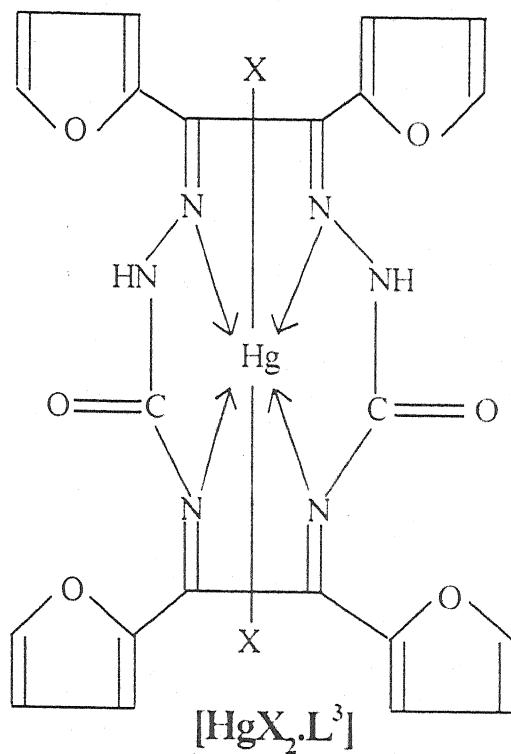
20	$\text{HgL}^6(\text{NO}_3)_2$	677.6	571.6	401.4	402.8		403.8	532.2	-	-	-	202.4
21	L^7	-	-	399.4	-		400.8	-	533.6	-	-	-
22	$[\text{HgL}^7\text{Cl}_2]$	677.8	571.6	401.4	-		403.8	-	533.6	-	-	202.4
23	$\text{HgL}^7(\text{NO}_3)_2$	677.6	571.6	401.4	402.8		403.8	532.2	533.6	-	-	-
24	L^8	-	-	-	-		400.8	-	533.6	-	-	-
25	$[\text{HgL}^8\text{Cl}_2]$	677.8	571.6	-	-		403.8	-	533.6	-	-	202.4
26	$\text{HgL}^8(\text{NO}_3)_2$	677.6	571.6	-	402.8		403.8	532.2	533.6	-	-	-
27	L^9	-	-	-	-		399.8	400.8	-	533.6	-	-
28	$[\text{HgL}^9\text{Cl}_2]$	677.8	571.6	-	-		399.8	403.8	-	533.6	-	202.4
29	$\text{HgL}^9(\text{NO}_3)_2$	677.6	571.6	-	-		399.8	403.8	532.2	533.6	-	-



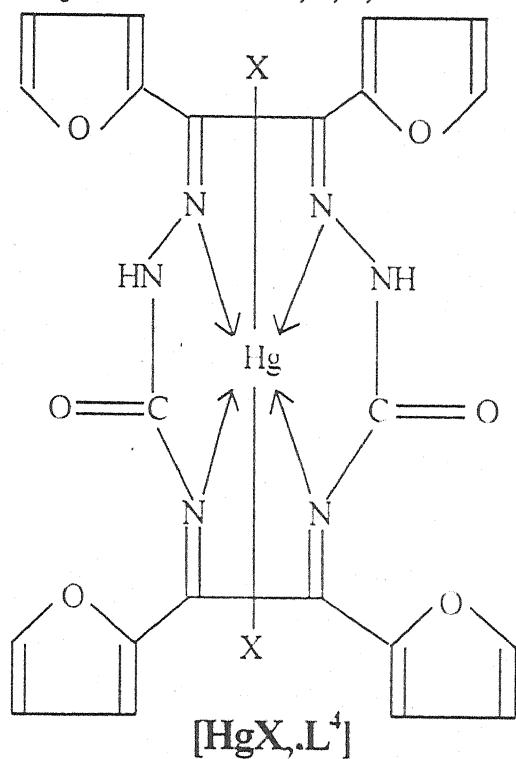
$L^1 = 5,11\text{-diethyl-6,12-dimethyl-3,8-dione-1,2,4,7,9,10\text{-hexaazacyclododeca-1,4,6, 10\text{-tetraene}}$



$L^2 = 5,11\text{-diethyl-6,12-dimethyl-3,8-dione-1,2,4,7,9,10\text{-hexaazacyclododeca-1,4,6, 10\text{-tetraene}}$

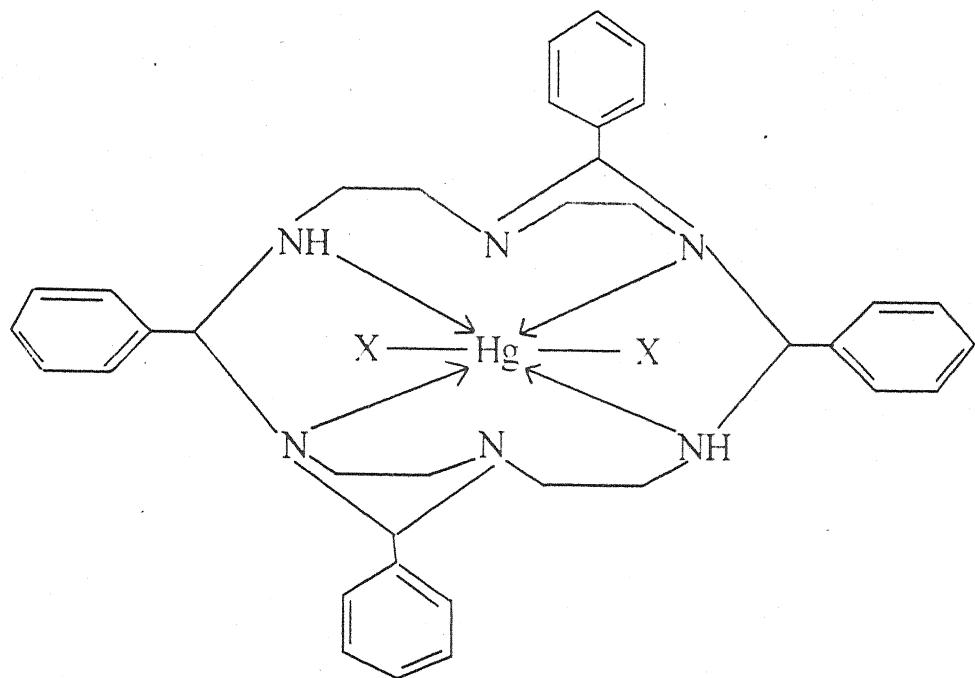


$\text{L}^3=5,6,11,12\text{-tetrafuryl3,8-dione-1,2,4,7,9,10-}$
 $\text{hexaazacyclododeca-1,4,6, 10-tetraene}$

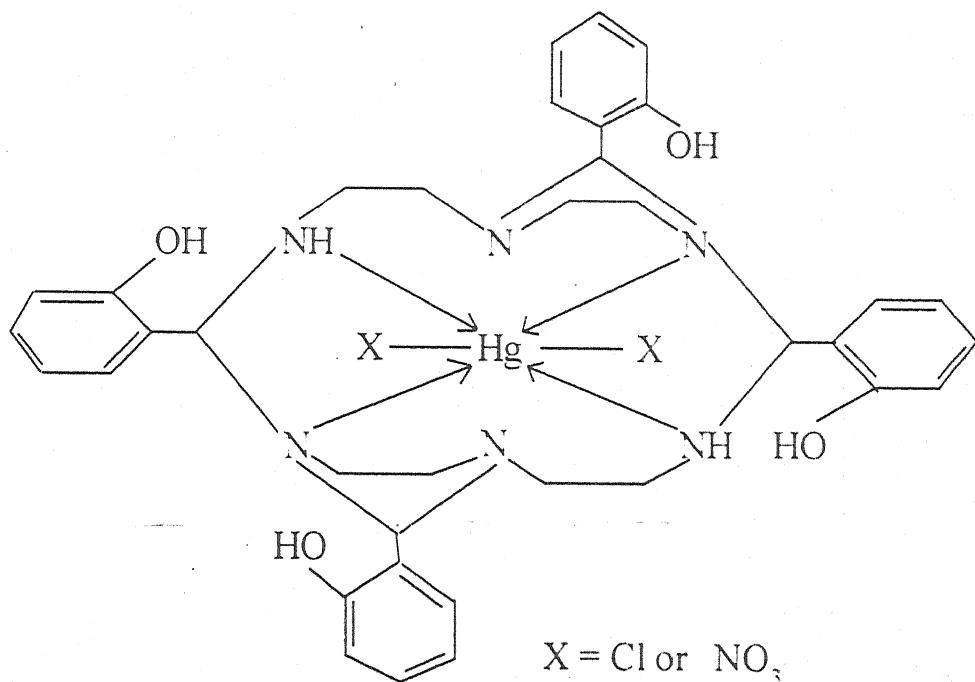


$\text{L}^4=5,6,11,12\text{-tetrafuryl3,8-dione-1,2,4,7,9,10-}$
 $\text{hexaazacyclododeca-1,4,6, 10-tetraene}$

Fig 8

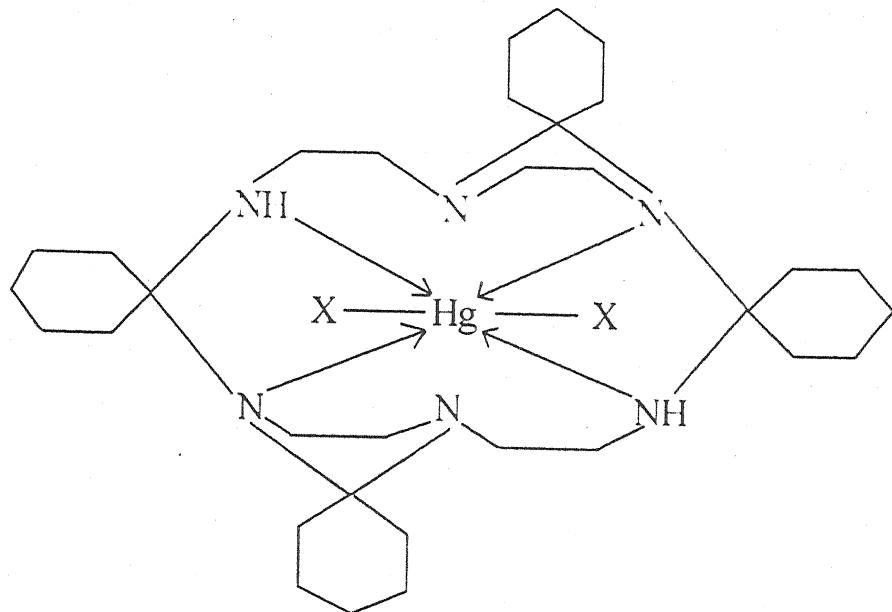


Structure of $[\text{HgX}_2.\text{L}^5]$
 $\text{L}^5 = 2,7,9,14\text{-tetraphenyl-1,3,6,8,10,}$
 $13\text{-hexaazacyclooctadecane}$

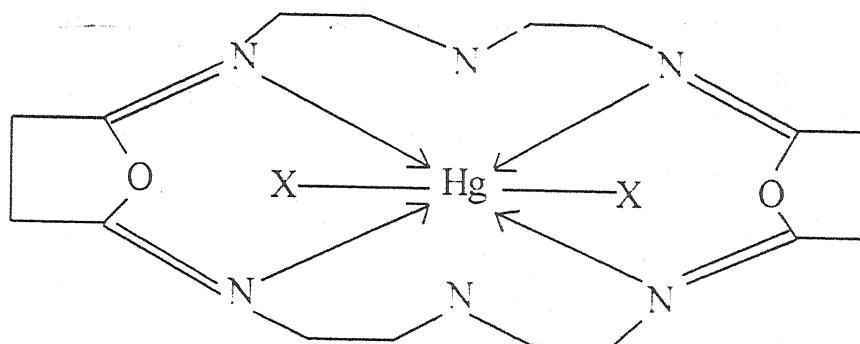


Structure of $[\text{HgX}_2.\text{L}^6]$
 $\text{L}^6 = 2,7,9,14\text{-tetra hydroxy phenyl-}$
 $1,3,6,8,10,13\text{- hexaazacyclooctadecane}$

Fig. 9

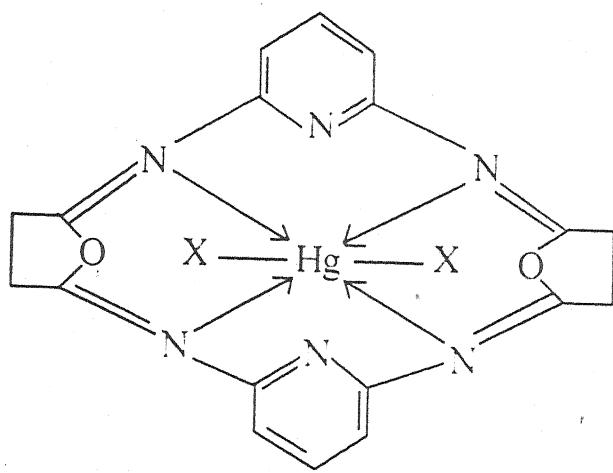


$X = \text{Cl or } \text{NO}_3$
 Structure of $[\text{HgX}_2 \cdot \text{L}^7]$
 $\text{L}^7 = 2,7,9,14\text{-tetra cyclohexyl-1,3,6,8,10,13-}$
 hexaazacyclooctadecane



$X = \text{Cl or } \text{NO}_3$
 Structure of $[\text{HgX}_2 \cdot \text{L}^8]$
 $\text{L}^8 = 23,24\text{-dioxo-1,6,9,12,17,20-}$
 hexazacyclotetracosa- 1,5,12,16-tetraene

Fig - 10



$X = \text{Cl or } \text{NO}_3$
 Structure of $[\text{HgX}_2 \cdot \text{L}^9]$
 $\text{L}^9 = 25,26\text{-dioxo-1,6,12,17,23,24-}$
 hexaazacyclohexacosa- 1,5,12,16-tetraene

Fig - 11

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CHAPTER - V

Result & Discussion

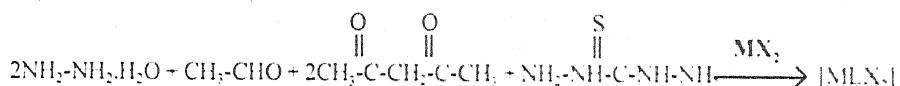
Synthetic macrocyclic complex of transition metals are attracted much attention as promising objects in coordination and supramolecular chemistry [1]. The chemistry of transition metal macrocycles is extensive because of their close relationship to molecules of biological significance [2-5]. The importance of these complexes is due to the role they play as models for protein metal binding sites in biological systems, as synthetic ionophores [6], electro catalyst in fuel cells [7], MRI contrast agents [8-9], luminescent sensors [10], as anticancer drug [11] and as radio immunotherapeutic agents [12]. These extensive application have been worth interesting to design new macrocyclic ligands for biological & industrial applications. Coordination compounds containing macrocyclic ligands have been studied during the past decades owing to their wide applications in biological and sensor fields [13,14].

In the past decades a great attention has been devoted to design and synthesize Schiff bases with enhanced ability to selectively encapsulate the given metal ion [15,16]. A large number of macrocycles [17,18] and their complexes with transition metal ion have been synthesized and characterized. Several macrocyclic ligands derived from

hydrazine, thiocarbohydrazine precursors have been reported [19, 20]. A literature survey reveals that very few Hg (II) macrocyclic complexes have been prepared [21-27]. In the present chapter the synthesis and characterization of Hg [II] octaazamacrocyclic complexes, $[MLX_2]$ {M= Hg(II) and [X=Cl or NO_3^-]} obtained by the template condensation reaction of hydrazine, acetaldehyde, acetyl acetone, benzoylacetone, dibenzoylmethane and thiocarbohydrazide

RESULT AND DISCUSSION

A series of octaazamacrocyclic complexes $[MLX_2]$ have been synthesized by the template condensation of hydrazine, acetaldehyde, acetyl acetone and thiocarbohydrazine with metal ions in a 2:1:2:1:1 molar ratio may be represented by the following reactions :



Where M = Hg (II); X = Cl, NO_3^-

All complexes are stable to the atmosphere and have

shown high melting points. Elemental analyses were within $\pm 0.5\%$ for C, H and N and the low molar conductance values of all the compounds in DMSO at room temperature, which supports [28] the contention that the nature of these complexes are non-ionic (Table 1). However, we could not grow single crystals suitable for x-ray crystallographic studies.

The IR spectrum does not exhibit any band corresponding to the free amino and ketonic groups. A new weak band appeared in the $1580-1620\text{ cm}^{-1}$ region in the IR spectra of all the complexes which may be assigned to the imine ν ($\text{C}=\text{N}$) stretching vibration [29]. This is in support of the formation of the azomethine group during the condensation. This range of ν ($\text{C}=\text{N}$) vibrations is in the region reported for the coordinated $\text{C}=\text{N}$ [30] group. The medium intensity bands appeared in the $410-445\text{ cm}^{-1}$ region are assignable [31] ν (Hg-N) vibrations. The appearance of the sharp single band in the $3210-3248\text{ cm}^{-1}$ region assignable to the condensed N-H group [32] and the absence of bands characteristics of the NH_2 group of the hydrazine moiety support the proposed condensation. This is further confirmed by the appearance of a

characteristic ν (C-N) band around 1160-1200 cm^{-1} . The coordination of the nitrato and chloro groups has been ascertained by bands in the 235-255 & 255-310 cm^{-1} region which may be reasonably be assigned [31-33] to ν (Hg-O) and ν (Hg-Cl).

The photoelectron binding energy (BE) data of all metal ions $\text{Hg } 4p_{3/2,1/2}$ $\text{Cl } 2p$ and $\text{N } 1s$ for HgCl_2 , $[\text{HgLCl}_2]$ and $[\text{HgL}(\text{NO}_3)_2]$ (where M= Hg (II)) are listed in table 2. It may be seen that the $\text{Hg } 4p_{3/2,1/2}$ photoelectron peak BE values were observed higher in metal salts than in the metal complexes (fig 1-2) suggesting that the metal ions have higher electron density in the metal complexes than the metal salts due to involvement of the metal ions in coordination. Further, the $\text{N } 1s$ photoelectron peak have shown two BE values for all these metal complexes 399.4 eV and (402.6-402.8 eV) than the free nitrogen atom (~399 eV) one for nitrogen from -NH group and other for nitrogen from -C=N group. The higher $\text{N } 1s$ binding energy value ~ (402.6-402.8 eV) suggest a more effective positive charge on the nitrogen atom of -C=N group in the metal complexes [34]. From these $\text{M } 2p_{3/2}$ and $\text{N } 1s$ XPS data one can conclude that the nitrogen atom in these metal complexes is

coordinated to metal ion [34]. Furthermore, in case of $[\text{HgL}(\text{NO}_3)_2]$ complexes three nitrogen peaks were observed in the range of 399.4 eV; 402.6-402.8 eV and 408.4-408.6 eV in 2: 2: 1 intensity ratio, out of these three N $1s$ photoelectron peaks, one N $1s$ photoelectron peak with low intensity (BE=408.4-408.6 eV) with higher BE should be due to the NO_3 group and may be assigned to be in inner-sphere coordination [34]. The C $12p$ photoelectron peak of $[\text{HgLCl}_2]$ complexes have shown higher BE values in the range of 201.2-201.4 eV than the starting materials HgCl_2 (table 2), which suggest that in all the metal complexes chloride ion is coordinated in the inner coordination sphere of the metal ion. (Fig 3-6)

The S $2p$ photoelectron BE were found same in all metal complexes $[\text{HgLCl}_2]$ and $[\text{HgL}(\text{NO}_3)_2]$ as in thiocarbohydrazide, suggesting non-involvement of sulphur atom in coordination.

EXPERIMENTAL

The metal salts HgCl_2 and $\text{Hg}(\text{NO}_3)_2$ (X=Cl or NO_3) (all BDH) were commercially available pure samples. The chemicals hydrazine monohydrate, 2,4- pentanedione

(Fluka) benzoylacetone dibenzoylmethane acetaldehyde (BDH) and thiocarbohydrazide (Alfa Aesar) were used as received. All solvents were reagent grade and purified as described elsewhere prior to use [35].

Characterization of the complexes -

Elemental analyses were obtained at the microanalytical laboratory of CDRI, Lucknow, India. Metals and chloride were determined volumetrically [39] and gravimetrically [40] respectively. The IR spectra (4000-200cm⁻¹) of all prepared complexes were recorded as CsI disc on a Perkin-Elmer 621 spectrophotometer. The electrical conductivity of 10⁻³ M solution in DMSO was obtained on Digisum Electronic conductivity Bridge at room temperature. The x-ray photoelectron spectra were recorded on a V.G. Scientific ESCA-3MK II electron spectrometer. The Mg K α X-ray line (1253.6 eV) was used for photo-excitation. The Cu 2P_{3/2} (BE = 932.8±0.2) & Au 4F_{7/2} (BE=83.8±0.1) lines were used to calibrate the instrument and Ag 3d_{5/2} (BE = 368.2) was used for cross checking [34]. All the spectra were recorded using the same spectrometer parameter of 50 eV pass energy and 4 mm slit width. The reduced full width at half height maximum

(FWHM) at the Au $4f_{7/2}$ (BE = 83.2 eV) level under these conditions was 1.2 eV. The powdered sample was mixed with high purity silver powder to reduce the charging effect. A thin layer of such a sample was pressed on gold metal gauze, which was welded to a nickel sample holder. The Ag $3d_{5/2}$ level (Eb 368.2 eV) obtained from this sample was sharp and did not show any observable shift. Thus, the charging of the sample, if at all present, was negligible [34]. The spectra were recorded in triplicate in the region of interest. In most cases the binding energies were reproducible within ± 0.1 eV. The usual least-squares fitting procedure of determining peak positions, line widths and areas was used.

SYNTHESIS OF THE COMPLEXES

Synthesis of dichloro/ nitrato [2, 5, 8, 10, 13, 16-hexamethyl-3, 4, 6, 7, 11, 12, 14, 15-octa azacyclohexadecane-2, 7, 10, 15-tetraene] metal (II), [HgLX]₂ (M= Hg (II) X=Cl or NO₃)

In methanolic solution (25ml) of hydrazine hydrate (0.004 moles, 0.198 ml), a methanolic solution (25ml) of acetaldehyde (99%) (0.001 moles, 1.13mL) was added

dropwise and was stirred for 7 h. To this mixture a methanolic solution (25ml) of the metal salt (0.001 mole) was added followed by the addition of 2,4-pentanedione or benzoylacetone or dibenzoyl methane (0.002 moles, 0.21mL) and hot solution of thiocarbohydrazide (0.001, mL). The resulting mixture was refluxed for 9 h until a precipitate appeared which was filtered, washed thrice with methanol and dried over calcium chloride in *vacuo*. The purity of the final product was checked by TLC on silica Gel-G of the complexes in DMSO solution using anhydrous methonal (50%) , and tetrahydrofurance (50%) as eluent. Only one spot was observed in each case after developing in an iodine chamber, indicating that the complexes were pure.

On the basis of all of the above mentioned results the proposed structure of $[\text{HgLX}_2]$ complexes may be assigned as shown in (Fig. 7).

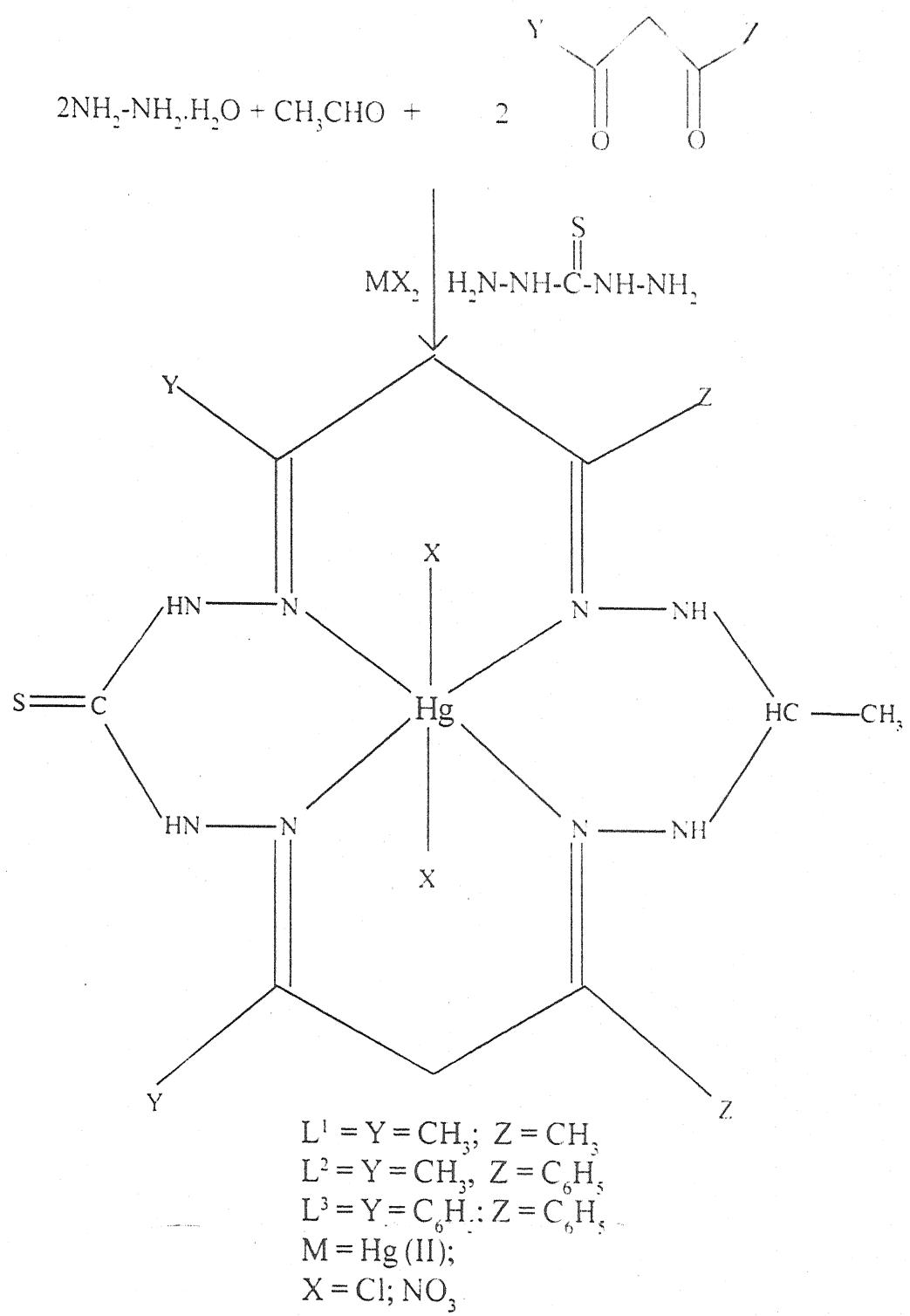


Figure 7. Template synthesis of 16- membered metal complexes.

**Table 1 : Elemental Analysis and molar conductivity of
[HgLX₂] complexes where L=1,2 & 3; X = Cl, NO₃**

Sr	Compound	Found (calcd)%			Molar Conductivity ohm ⁻¹ cm ² mol ⁻¹ inDMF
		C	H	N	
1	HgL ¹ Cl ₂	23.2 (23.3)	3.0 (3.1)	19.6 (19.8)	18
2	HgL ¹ (NO ₃) ₂	22.4 (22.5)	3.2 (3.0)	27.0 (27.2)	16
3	HgL ² Cl ₂	40.2 (40.3)	3.6 (3.7)	15.0 (15.0)	20
4	HgL ² (NO ₃) ₂	39.0 (39.2)	3.4 (3.6)	18.2 (18.3)	12
5	HgL ³ Cl ₂	51.0 (51.2)	4.0 (4.1)	14.2 (14.4)	18
6	HgL ³ (NO ₃) ₂	44.0 (44.2)	3.4 (3.5)	15.4 (15.6)	22

Table - 2 : Hg $4p_{1/2,3/2}$, N1s, S2p and Cl2p binding energies in salt, ligands and HgL₂X₂ complexes
(where L=1, 2 & 3; X = Cl, NO₃)

Sr. No.	Salt ligand & Complex	Hg metalion			N 1s			O 1s			S2p		Cl2p	
		Hg4p _{1/2}	Hg4p _{3/2}	N _(NH)	N _(NO₃)	N _{C≡N}								
1	HgCl ₂	6788	572.8	-	-	-					-	-	201.2	
2	Hg(NO ₃) ₂	678.6	572.6	-	400.2	-	532.8	-	-		-	-	-	
3	L ¹	-	-	399.4	-	400.8	-		166.6	-			-	
4	HgL ¹ Cl ₂	677.8	571.6	399.4	-	403.8	-		166.6		202.4			
5	HgL ¹ (NO ₃) ₂	677.6	571.6	399.4	402.8	403.8	532.8	166.6	-				-	
6	L ²	-	-	399.4	-	400.8	-		166.6		-		-	
7	HgL ² Cl ₂	677.6	571.6	399.4	-	403.8	-		166.6		202.4			
8	HgL ² (NO ₃) ₂	677.6	571.6	399.4	402.8	403.8	532.8	166.6	-				-	
9	L ³	-	-	399.4	-	400.8	-		166.6		-		-	
10	HgL ³ Cl ₂	677.6	571.6	399.4	-	403.8	-		166.6		202.4			
11	HgL ³ (NO ₃) ₂	677.6	571.6	399.4	402.8	403.8	532.8	166.6	-				-	

Hg $4p_{1/2}$ photoelectron peak

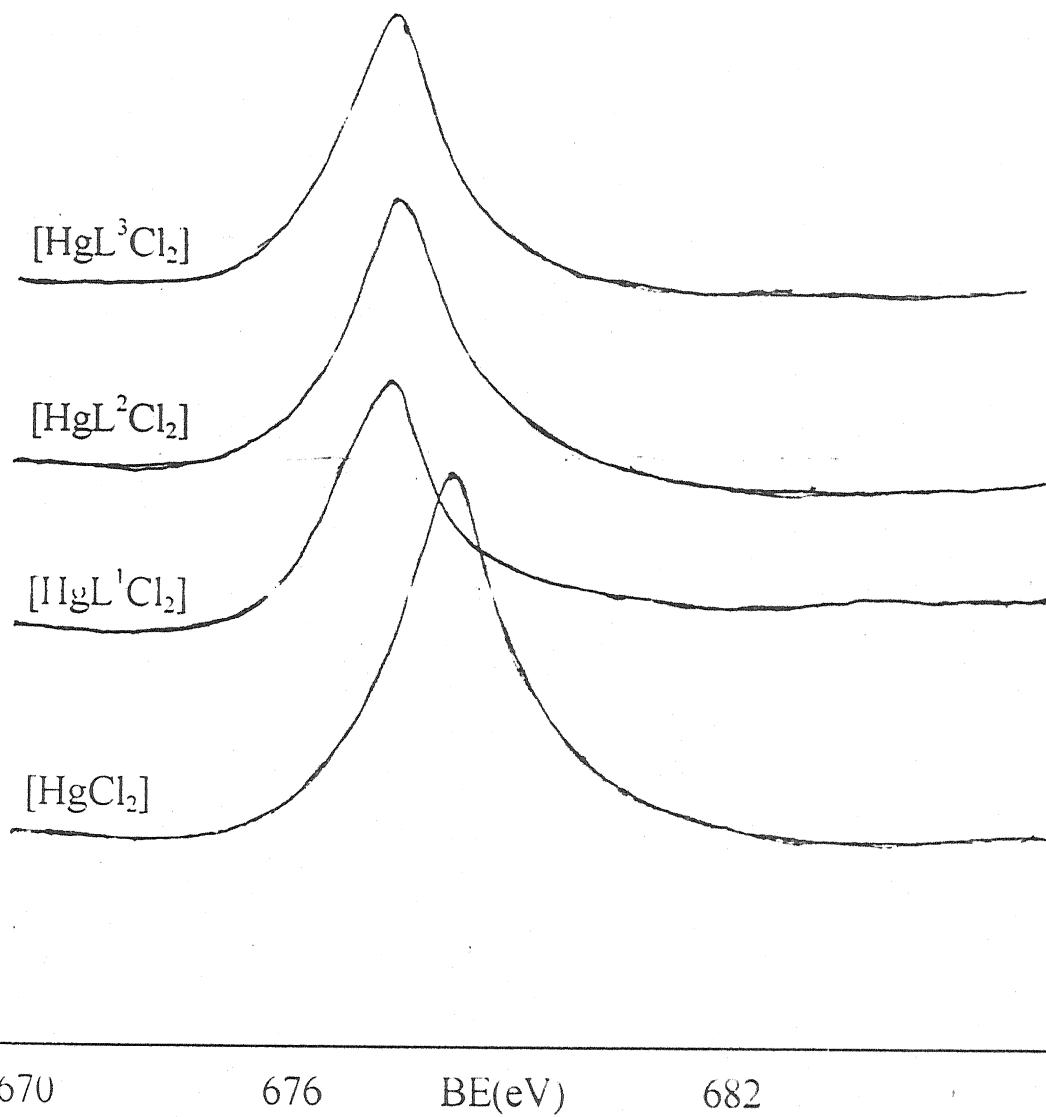


Fig 1 : Hg $4p_{1/2}$ binding energies (eV) in HgCl_2 and HgLCl_2 complexes

Hg $4p_{1/2}$ photoelectron peak

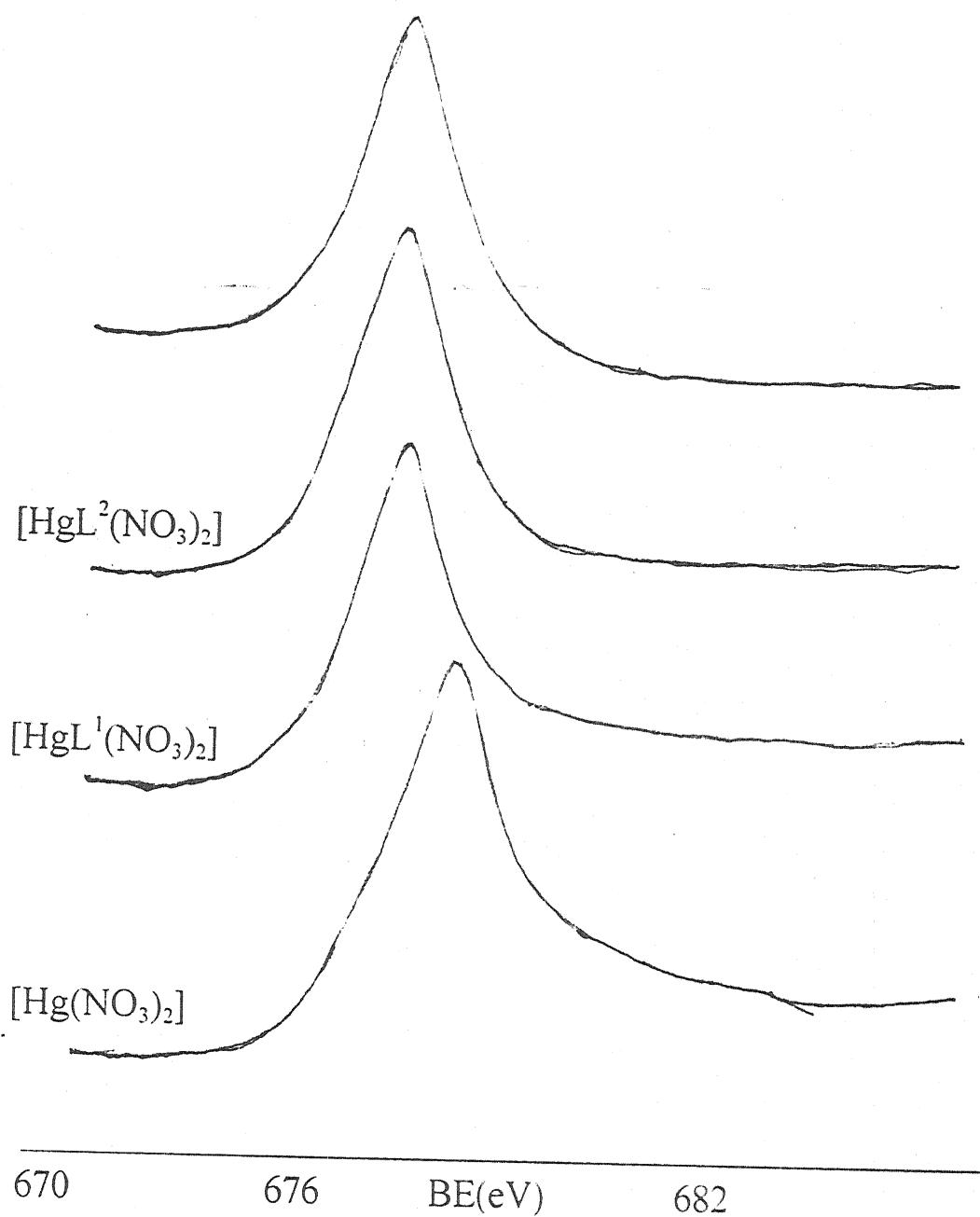


Fig 2 : Hg $4p_{1/2}$ binding energies (eV) in
 $Hg(NO_3)_2$ and $HgL(NO_3)_2$ complexes

N1s photoelectron peak

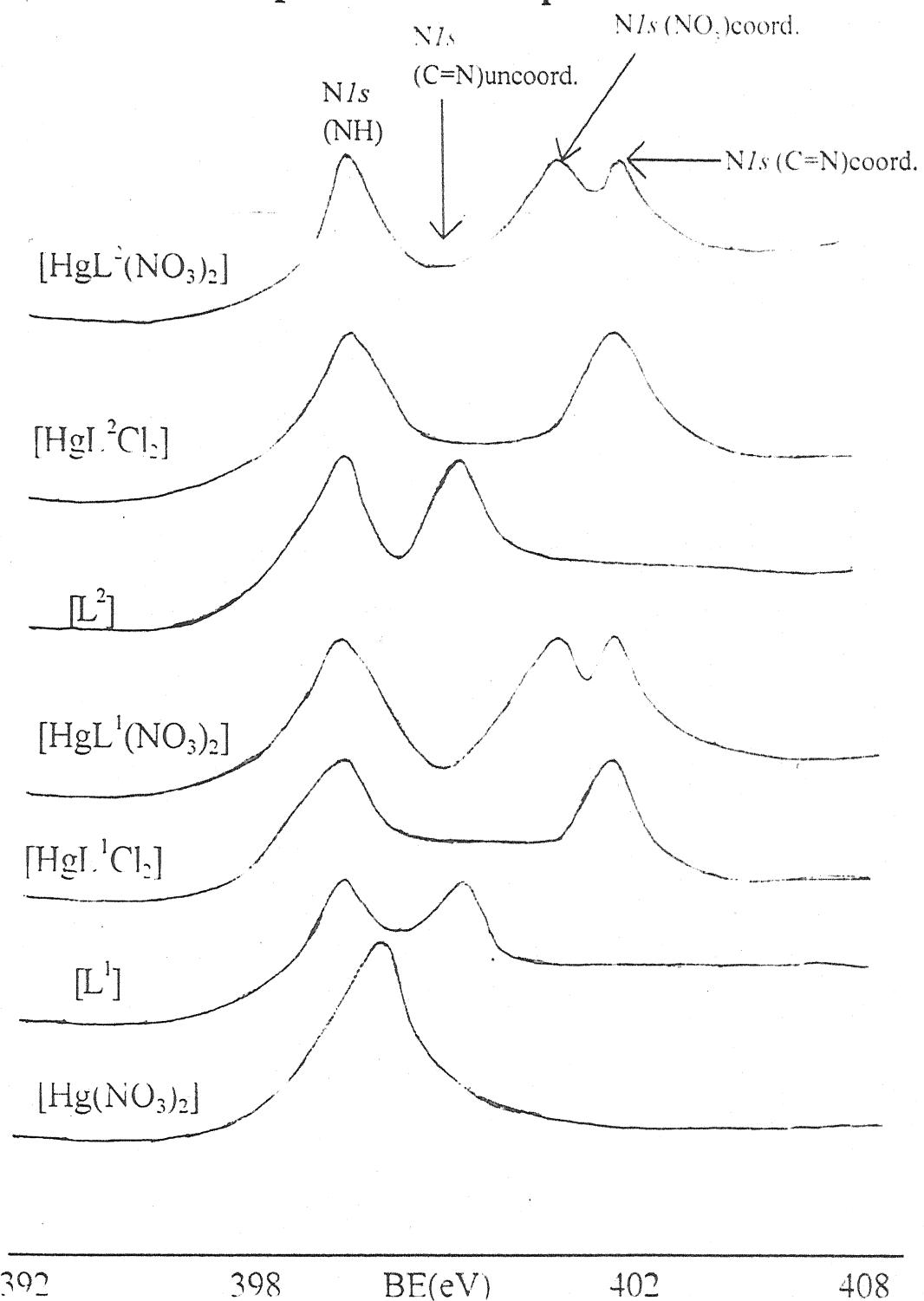


Fig 3 : N1s binding energies (eV) in $\text{Hg}(\text{NO}_3)_2$;
Ligand (L^1 & L^2) and $[\text{HgLX}_2]$ complexes

O1s photoelectron peak

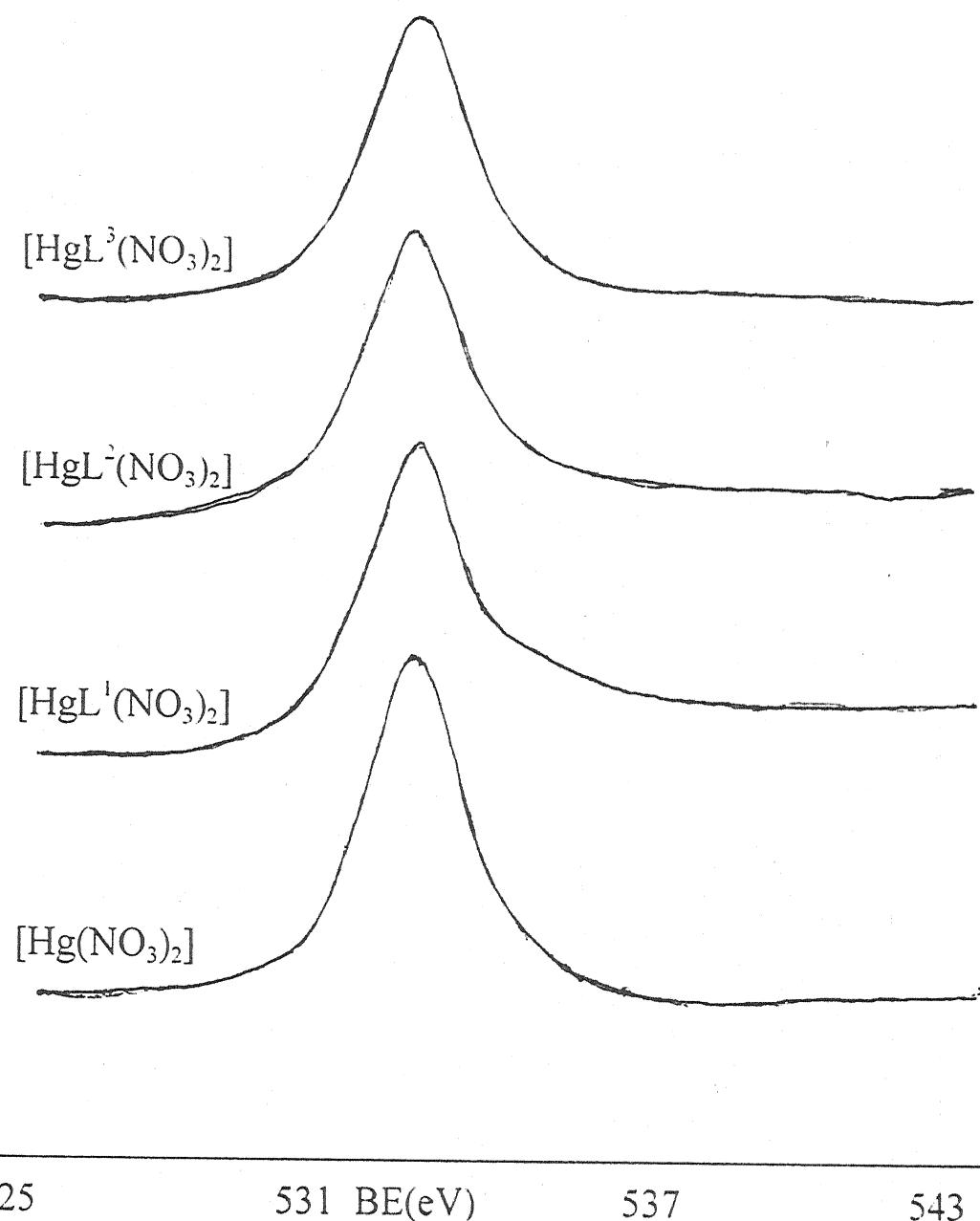


Fig 4 :O1s binding energies (eV) in $\text{Hg}(\text{NO}_3)_2$ and $\text{HgL}(\text{NO}_3)_2$ Complexes

S 2p photoelectron peak

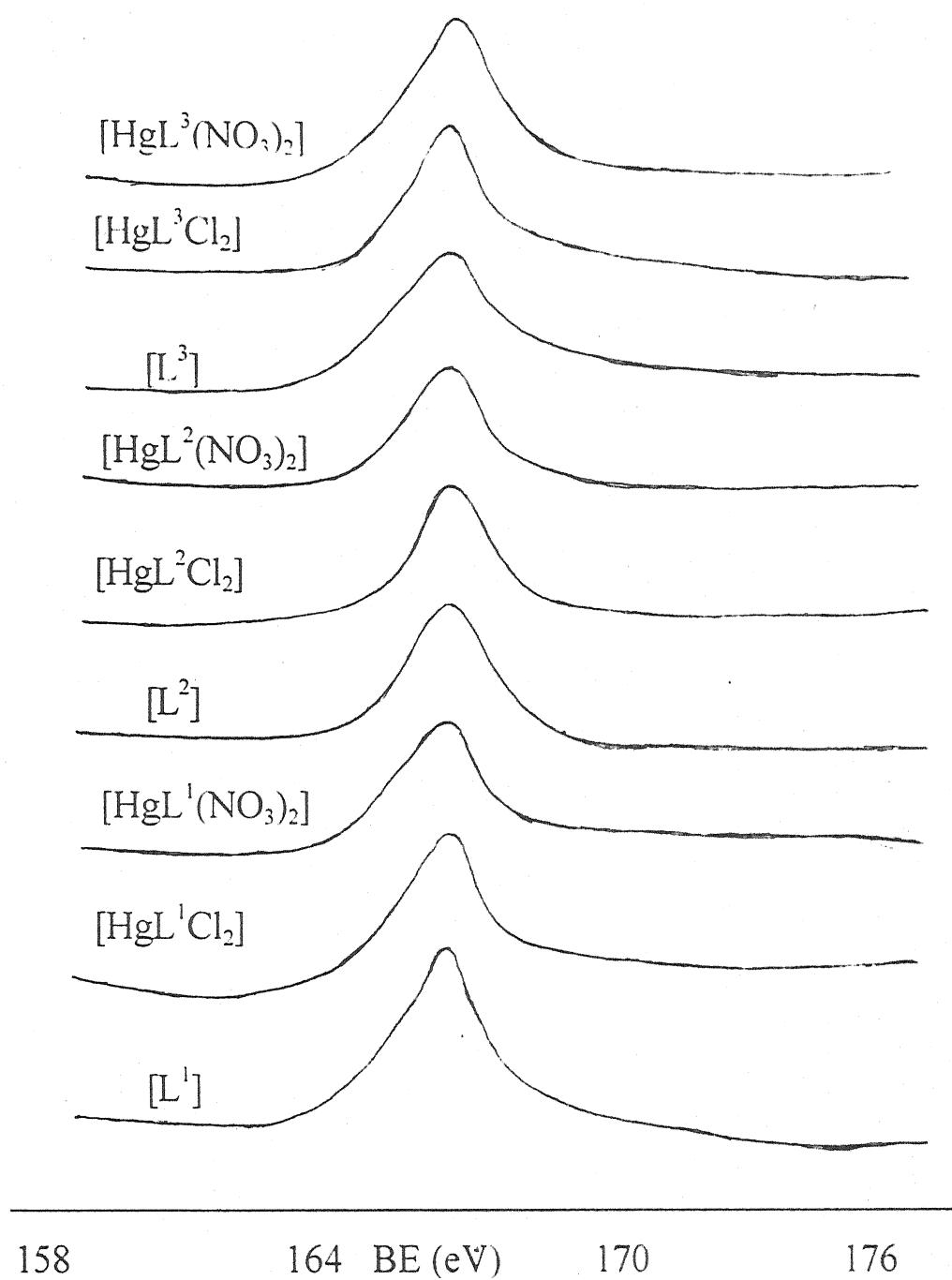


Fig 5 :S2p binding energies (eV) in Ligands and
[HgLX₂] Complexes

Cl 2p photoelectron peak

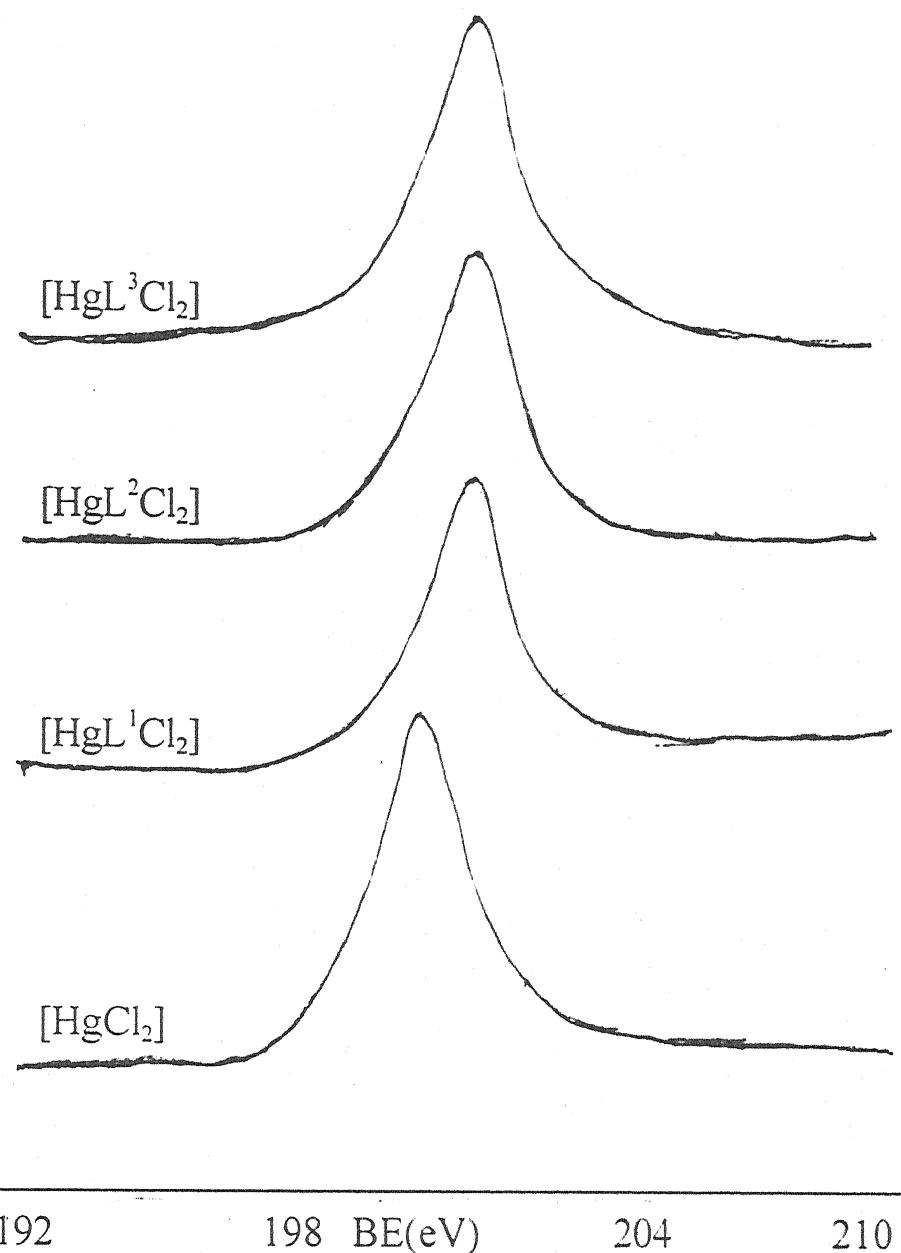


Fig 6 :Cl 2p binding energies (eV) in HgCl_2 and $[\text{HgLCl}_2]$ Complexes

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CHAPTER - VI

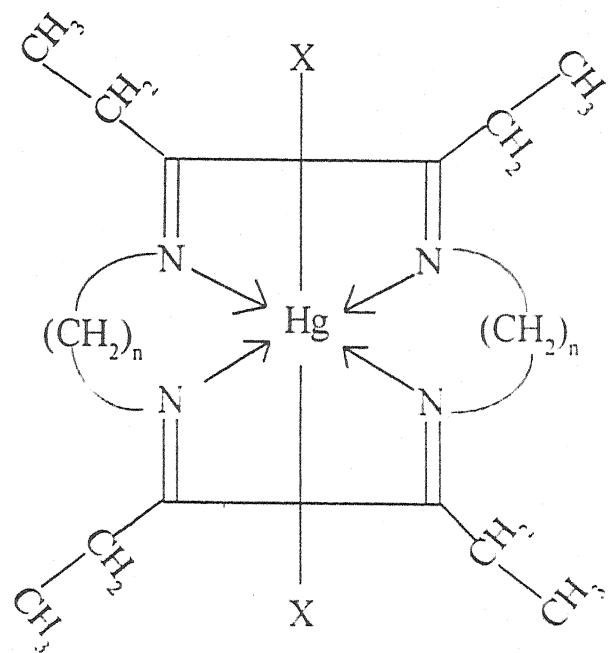
Conclusion

Mercury, which has symbol Hg, atomic number 80, electronic configuration $1s^2, 2s^2p^6, 3s^2p^6d^{10}, 4s^2p^6d^{10}f^{14}, 5s^2p^6d^{10}, 6s^2$, belong to II B group of periodic table and it has stable oxidation state +1 and +2. Many scientific pieces of equipment depend for their working on mercury's unique combination of properties among these are thermometers, barometers, gas and pressure, regulators, method gauges, toepler pumps, temperature compensating, pendulums, diffusion pumps, standard cells and mercury electrodes. Industrially, mercury is used to fill fluorescent tubular lamps, high pressure street lamps, a.c. rectifiers and thyratrons.

The coordination chemistry of multidentate macrocycles has been a field of intensive research over the past many years. A macrocycle is defined as cyclic compound having at least nine or more, heteroatomic members and with three or more, donor centres¹⁻⁴.

Condensation of primary diamine with haloalkanes has played a vital role in the development of synthetic macrocyclic ligands, which have been proved to be a fruitful source of tetraazamacrocycles. A literature search revealed⁵⁻¹¹ that a few number of tetraazamacrocyclic Hg(II)

complexes have been prepared and characterised but no work has been done on Hg(II) complexes of macrocycles derived from 1,3- diaminopropane; 1,4 – diaminobutane; 1,5-diaminopentane, 1,7-diaminoheptane; 1,8 diaminoctane; 1,9- diaminononane and 1,10-diaminodecane. In chapter III, such Hg(II) complexes with macrocyclic ligands have been synthesised and characterised on the basis of elemental analysis, molar conductivity, IR and XPS data, and established octahedral geometry and structure as shown below (Fig 1):



Where	L^1	=	$n = 3$
	L^2	=	$n = 4$
	L^3	=	$n = 5$
	L^4	=	$n = 7$
	L^5	=	$n = 8$
	L^6	=	$n = 9$
	L^7	=	$n = 10$
	X	=	Cl or NO_3

Fig 1 : Structure of $[HgL.X_2]$

Chapter IV deals with synthesis and characterisation of Hg (II) complexes with macrocyclic ligands i.e. $L^1=5,11$ -diethyl-6,12-dimethyl-3,8-dione-1,2,4,7,9,10-hexaazacyclododeca-1,4,6,10-tetraene; $L^2=5,11$ -diethyl-6,12-dimethyl-3,8-dithione-1,2,4,7,9,10-hexaazacyclododeca-1,4,6,10-tetraene; $L^3=5,6,11,12$ -tetrafuryl-3,8-dione-1,2,4,7,9,10-hexaazacyclododeca-1,4,6,10-tetraene; $L^4=5,6,11,12$ -tetrafuryl-1,3,8-dithione-1,2,4,7,9,10-hexaazacyclododeca-1,4,6,10-tetraene; $L^5=2,7,9,14$ -tetraphenyl-1,3,6,8,10,13-hexaazacyclooctadecane; $L^6=2,7,9,14$ -tetrahydroxyphenyl-1,3,6,8,10,13-hexaazacyclooctadecane; $L^7=2,7,9,14$ -tetracyclohexane-1,3,6,8,10,13-hexaazacyclooctadecane; $L^8=23,24$ -Dioxo-1,6,9,12,17,20-hexaazacyclo tetracos-1,5,12,16-teraeene and $L^9=25,26$ -Dioxo 1,6,12,17,23,24-hexaazacyclohexacosa-1,5,12,16-tetraene. All these $[HgLX_2]$ complexes where ($X=Cl; NO_3$) have been synthesised and characterised with elemental analysis molar conductivity, IR and XPS data and octahedral geometry was established with follow structure as shown below (Fig 2-10).

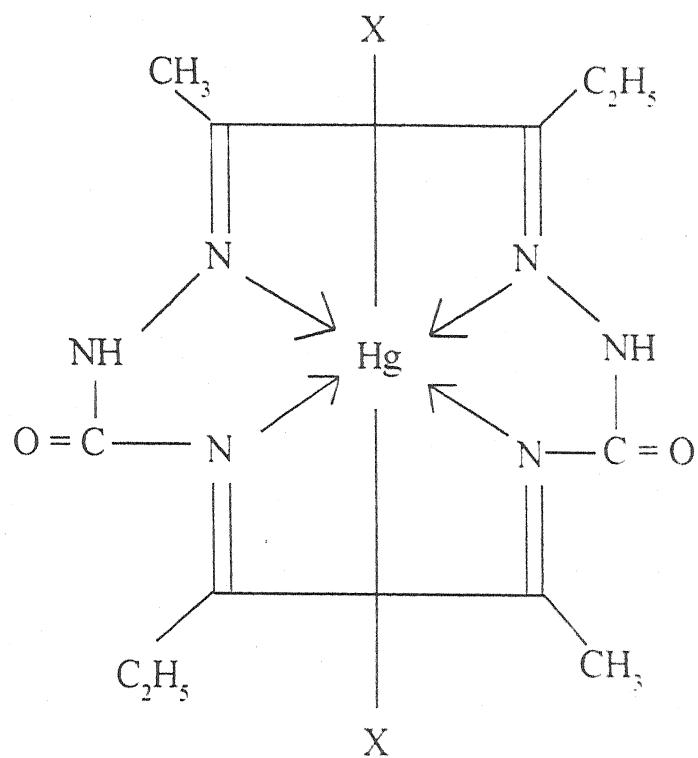


Fig 2 : $[\text{HgX}_2\text{.L}^1]$

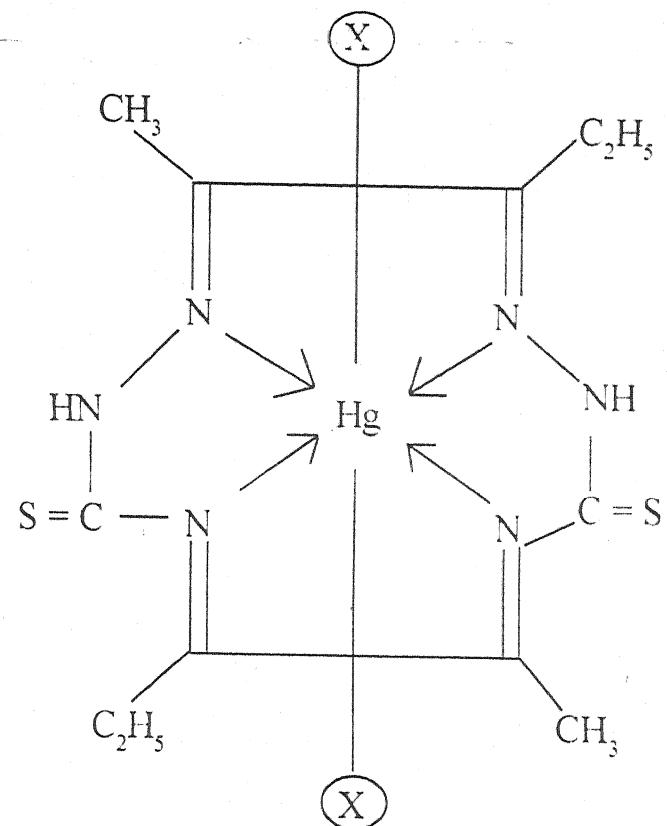


Fig 3 : $[\text{HgX}_2 \cdot \text{L}^2]$

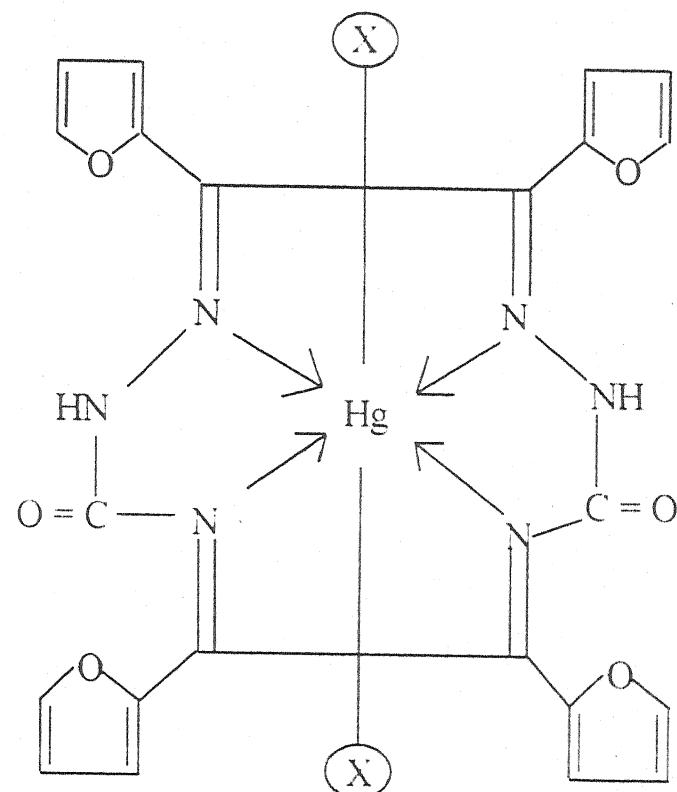


Fig 4 : $[\text{HgX}_2 \cdot \text{L}^3]$

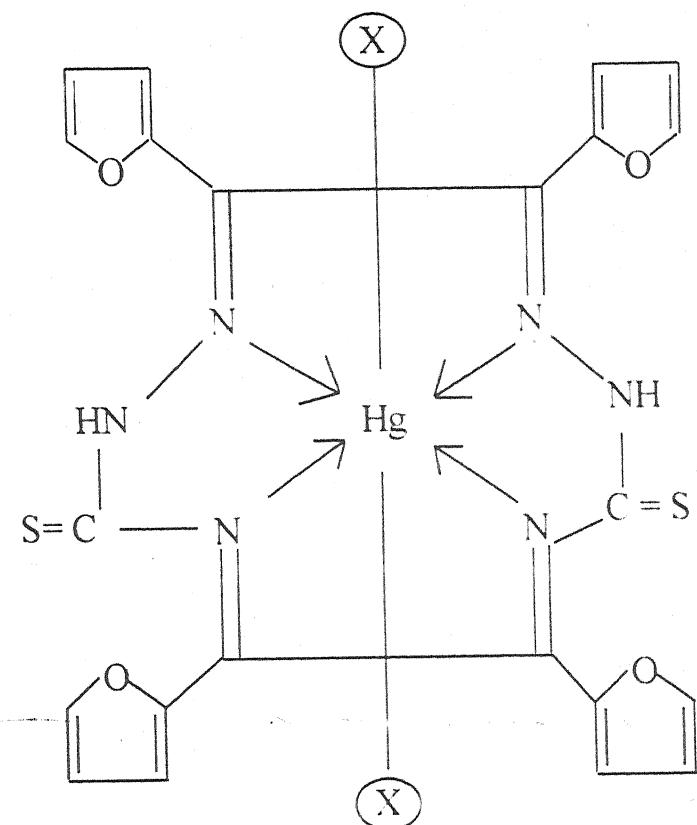


Fig 5 : $[\text{HgX}_2 \cdot \text{L}^4]$

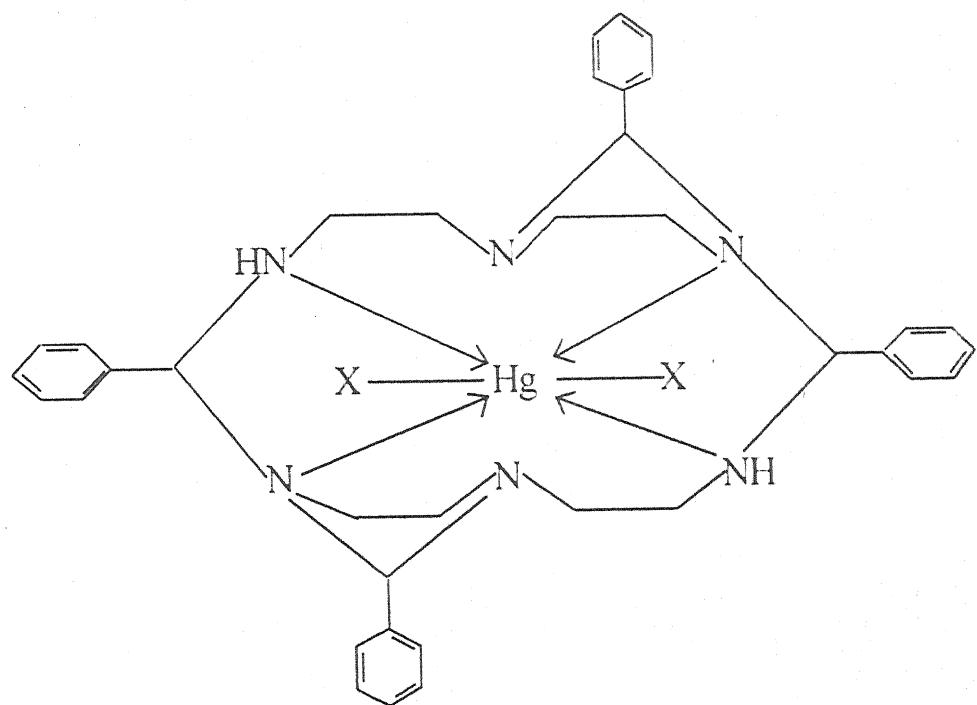


Fig 6 : $[\text{HgX}_2 \cdot \text{L}^5]$

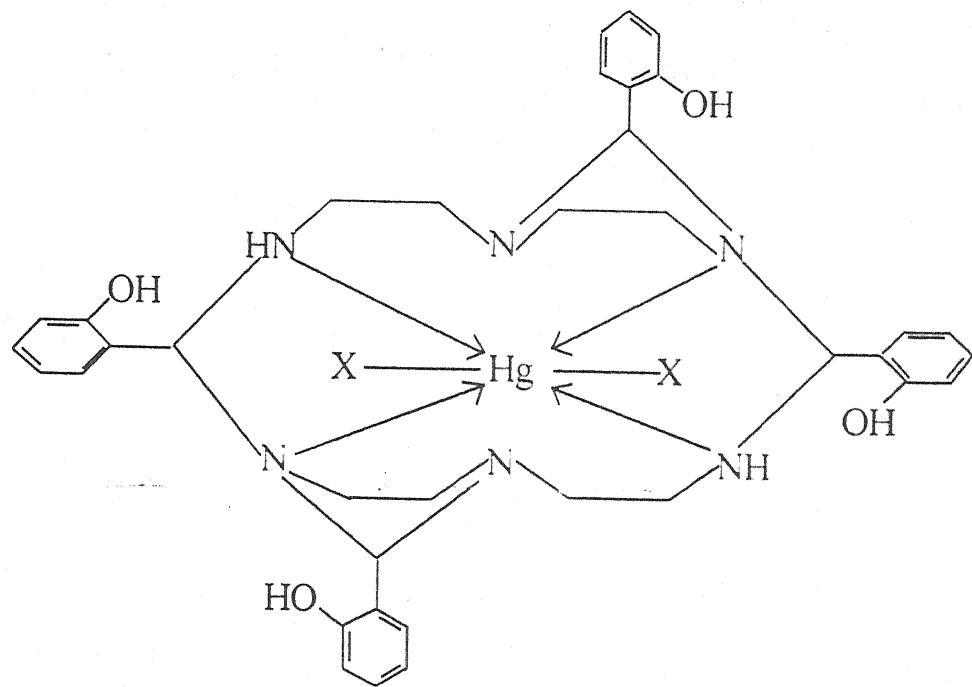


Fig 7 : $[\text{HgL}^6 \cdot \text{X}_2]$

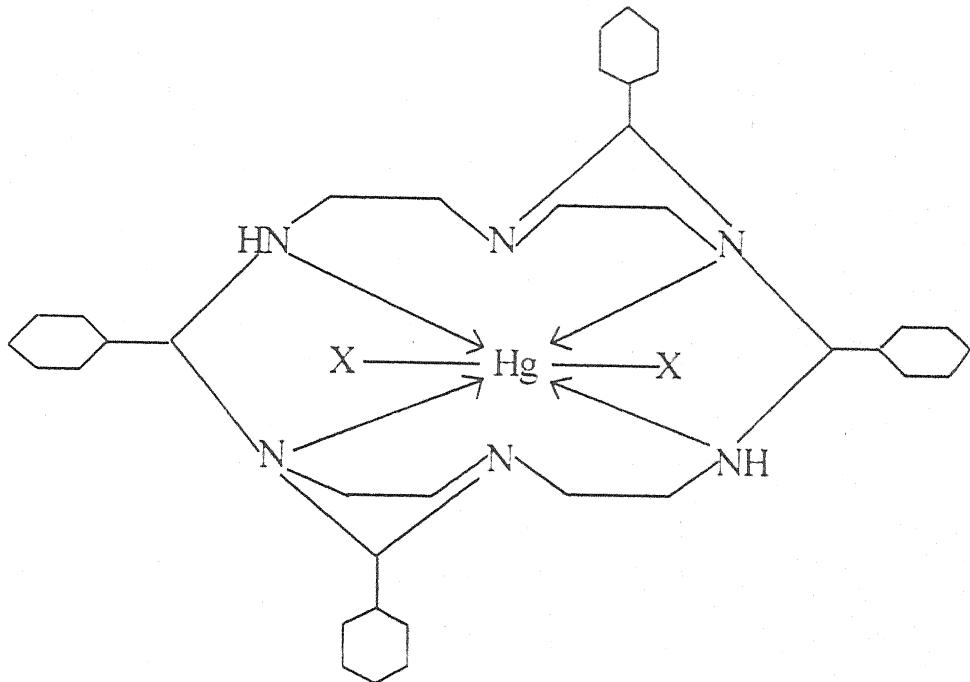


Fig 8 : $[\text{HgL}^7 \cdot \text{X}_2]$

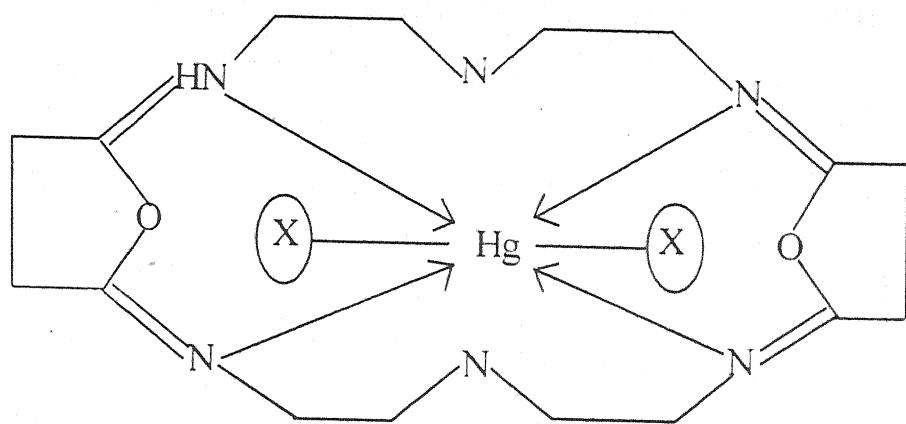


Fig 9 : $[\text{HgL}^8 \cdot \text{X}_2]$

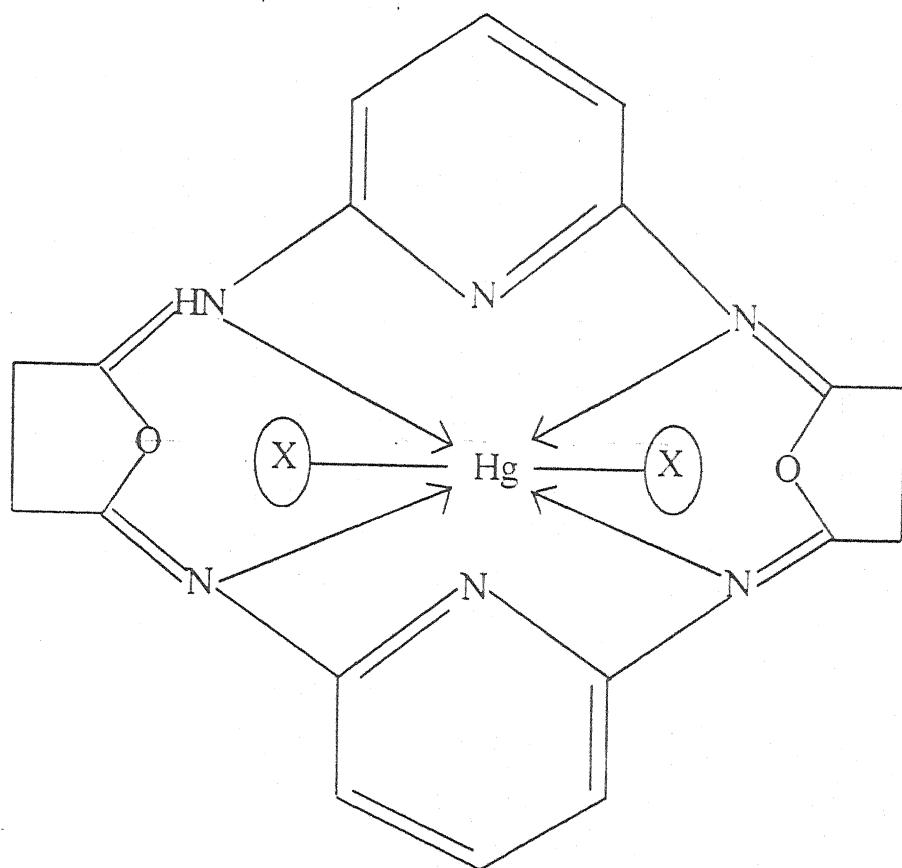


Fig 10 : $[\text{HgL}^9 \cdot \text{X}_2]$

Chapter V deals with the synthesis and characterisation of Hg(II) octaazamacrocyclic complexes $[MLX_2]$ ($X=Cl$; NO_3) obtained by the template condensation reaction of hydrazine, acetaldehyde, acetyl acetone, benzoylacetone, dibenzoylmethane and thiocarbohydrazide. These $[MLX_2]$ complexes have been synthesised and characterised by elemental analysis, molar conductivity, IR and XPS data, an octahedral geometry was established with following structure as shown in (fig 11).

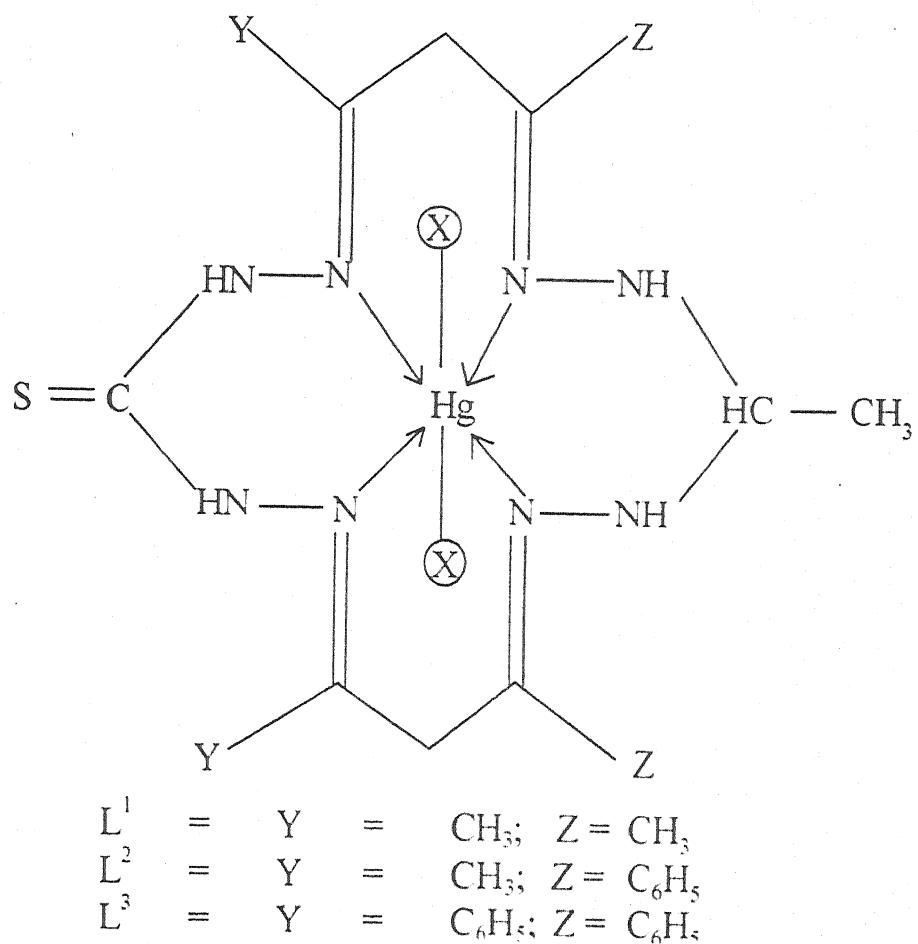


Fig 11 : $[HgL.X_2]$

The macrocyclic ligands and their complexes are interesting in view of their use as models to elaborate the metal ions interaction and to get an insight of the coordination sites in metalloproteins and in other biological systems¹²⁻¹⁴. These macrocyclic ligands also serve as models to study magnetic exchange phenomena. The macrocyclic ligands and their complexes have a diverse use in various fields. They are used as models for protein metal binding sites, pigments, vitamin B₁₂, photosynthesis, dioxygen, solution and potassium ion transport¹⁵⁻¹⁷. In biomedical systems¹⁸⁻²⁶ they are used as therapeutic reagents²⁷⁻³¹ in chelate therapy for the treatment of metal intoxication, as anti-HIV agents³²⁻³⁵ and as cyclic antibiotics whose antibiotic activity is because of specific metal complexation. Macroyclic complexes are also used as synthetic ionophores³⁶⁻³⁷ as requestering reagent for specific metal ions³⁸⁻³⁹, as chemical sensors⁴⁰⁻⁴⁷ in catalysis. They have rapid growing applications as radio-pharmaceuticals, contrast agents in magnetic resonance imaging⁴⁸⁻⁵¹ (MRI) and as luminescence sensors. These areas have led to a considerable effort in developing reliable in expensive synthetic routes for this category of compounds.

All these prepared Hg(II) complexes with macrocyclic ligands may also be useful in above mentioned fields.

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